Inorganica Chimica Acta, *166* (1989) 47–54

Electrochemical and Photophysical Properties of Mono- and Bimetallic Ruthenium(II) Complexes

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(Received May 9, 1989)

Abstract

Mono- and bimetallic complexes of ruthenium(II) containing 1,10-phenanthroline, and the bidentate, bridging ligands 2,3-bis(2′-pyridyl)pyrazine (dpp) or 2,3-bis(2′-pyridyl)quinoxaline (dpq) have been prepared and characterized. All of the mono- and bimetallic complexes, RuL_2BL^{2+} and $L_2RuBLRuL'_2{}^{4+}$ (L,L′ = bpy, phen; BL = dpp, dpq), emit in acetonitrile at room temperature and have excited-state lifetimes in the 20–300 ns range. The lowest energy absorption feature has been assigned as a metal-to-ligand charge-transfer (MLCT) band localized exclusively on BL (i.e. Ru(II) $d_\pi \rightarrow BLp_{\pi^*}$). Electrochemically, the potential of the Ru(III)/Ru(II) couple reflects the average ligand environment around the ruthenium center. There are numerous reductions that occur with each complex that are specific to the individual ligands with the reductions for the BLs (dpp and dpq) occurring at less negative potentials than for the L (bpy or phen) ligands. The positions of the absorption, emission and redox couples in these complexes are all consistent with a localized MLCT excited state and little metal–metal interaction in the isovalent Ru(II)/Ru(II) bimetallic complexes. The variety of metal/ligand combinations gives an assorted range of excited-state donor energies and excited-state redox couples. Oxidation of the excited-state species in general parallels the donor energy of the emissive state. Reduction of the excited-state species depends almost exclusively on the energy of the individual π^* LUMO in the ground state. The wide variety of excited-state donor energies and redox couples results in a series of complexes that have great potential for studying excited-state energy- and electron-transfer processes.

Introduction

The excited-state reactivity of complexes related to $Ru(bpy)_3{}^{2+}$ (where bpy = 2,2′-bipyridine) has received considerable attention because of the long lifetime of $Ru(bpy)_3{}^{2+*}$ in fluid solution at room temperature [1] and the ability of this moiety to undergo facile excited-state electron [1–6] or energy-transfer [7–11] reactions. The excited-state properties of $Ru(bpy)_3{}^{2+*}$ and the fact that this excited state is created by absorption of visible light, has placed this material as a prime candidate for solar energy cycles leading to water splitting or other usable solar energy driven reactions [12].

Previously, we expanded the capabilities of these complexes by the preparation and characterization of $Ru(dpp)_3{}^{2+}$ (where dpp = 2,3-bis(2′-pyridyl)pyrazine) [13]. Like the intensively studied $Ru(bpy)_3{}^{2+}$ center, $Ru(dpp)_3{}^{2+}$ absorbs visible light, has a long excited-state lifetime, and is stable thermally in both the oxidized and reduced forms of the complex. One advantage that $Ru(dpp)_3{}^{2+}$ has over $Ru(bpy)_3{}^{2+}$ is that the former is capable of binding an additional metal center to each dpp ligand to form thermally stable, polymetallic complexes [13].

In this report, we have prepared and studied the monometallic and bimetallic complexes of the type, $Ru(phen)_2(BL)^{2+}$ and $(phen)_2Ru(BL)RuL_2{}^{4+}$ (where phen = 1,10-phenanthroline; L = bpy, phen; BL = dpp or dpq (dpq = 2,3-bis(2′-pyridyl)quinoxaline)). Mono- and bimetallic complexes of dpp containing bpy ligands have been prepared and the electrochemistry, absorption and emission spectroscopies, and resonance Raman spectroscopy reported by Gafney and coworkers [14]. Rillema and coworkers [15] have studied some of the photochemistry, photophysics and electrochemistry of dpq complexes with bpy in place of phen.

The variation of the nature of BL and the nuclearity of the system has a tremendous effect on the ground-state redox potentials, the excited-state energies and lifetimes, and the ability of the system to undergo excited-state energy- or electron-transfer

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0020-1693/89/$3.50

quenching. The patterns that emerge indicate that optical and redox properties of polymetallic ruthenium complexes can be predicted and controlled synthetically.

Experimental

Materials

The ethanol, ether and toluene used in synthesis were analytical reagent grade and used without further purification. Water was deionized and then redistilled from alkaline permanganate in an all-glass apparatus. Acetonitrile used in electrochemical and photophysical measurements was purchased as spectroquality (Burdick and Jackson) from American Scientific Products and stored over molecular sieves. Potassium hexafluorophosphate (Alfa Inorganics) and tetrabutylammonium perchlorate (TBAP) (Fisher Scientific) were used as supplied. The ligand, phen (Sigma Chemical Co.), was used as supplied and dpp and dpq were prepared by the method of Goodwin and Lions [16]. Starting complexes for the preparation of mono- and bimetallic complexes were $Ru(phen)_2Cl_2$ and $R(bpy)_2Cl_2$ which were prepared by the modification [17] of the original procedure [18].

Synthesis

Monometallic complexes, $[Ru(phen)_2(BL)](PF_6)_2$

The monometallic complexes were prepared following the same general literature procedures in all cases [14, 15a]. Equimolar amounts (0.60 mmol) of $Ru(phen)_2Cl_2$ and dpp and dpq were mixed in 30–40 ml of a 3:1 (vol./vol.) ethanol/water mixture. The mixture was heated at reflux for 3 to 4 h for the dpp complex and approximately 24 h for the dpq complex. The crude product was precipitated from solution by the addition of a saturated, aqueous solution of KPF_6, and collected by filtration.

Both complexes were purified by column chromatography using alumina as the stationary phase and acetonitrile/toluene mixtures as the mobile phase. The crude complexes were dissolved in acetonitrile, placed on the column and eluted with 3:1 and 1:1 toluene/acetonitrile (vol./vol.) mixture. The dpp complex came off as a yellow–orange band while the dpq complex was a deeper orange. The eluant was reduced in volume to 10 ml and was added to ether to precipitate the complexes. The complexes were collected on a sintered glass filter, washed with ether, and dried under vacuum. Elemental analysis (Atlantic Microlabs, Atlanta, GA) showed excellent agreement with theoretical values (see ‘Supplementary Material’).

Bimetallic complexes, $[(phen)_2Ru(BL)RuL_2](PF_6)_4$

The symmetrical bimetallic complexes (L = phen) were prepared by mixing two equivalents (0.60 mmol) of $Ru(phen)_2Cl_2$ with one equivalent of dpp or dpq in 10–15 ml of a 3:1 (vol./vol.) ethanol/water mixture [14a, 15a]. The dpp solution was heated at reflux for ~24 h while the dpq solution required ~72 h. The unsymmetrical bimetallic complexes were prepared by mixing equimolar (0.60 mmol) amounts of $[Ru(phen)_2(BL)](PF_6)_2$ and $Ru(bpy)_2Cl_2$ in 20–30 ml of 3:1 (vol./vol.) ethanol/water. Once again, 24 h at reflux was used for the dpp complex and 72 h at reflux for the dpq complex. All products were precipitated by the addition of aqueous, saturated KPF_6 and collected by filtration.

Bimetallic complexes were purified by column chromatography using alumina as the stationary phase. The bimetallic complexes of dpp eluted as a purple–maroon band with 1:5 (vol./vol.) methanol/acetonitrile after any monometallic impurity had come off the column. The bimetallic dpq complexes came off the column as a blue–green band with acetonitrile after all monometallic complexes had been removed.

The product solutions obtained from column chromatography were reduced in volume to ~10 ml and precipitated by addition to ether. The products were collected by filtration, washed with ether and dried under vacuum.

Absorption Spectra

Absorption spectra were recorded at room temperature on a Bausch-Lomb Spectronic 2000 using gravimetrically prepared samples in acetonitrile.

Emission Spectra

Emission spectra were recorded at room temperature in acetonitrile using a SPEX Industries Model 5 spectrofluorometer. The emission maxima reported were uncorrected for detector response to maintain relative comparisons in the series of complexes. This was necessitated by the fact that the emission spectra of the bimetallic dpq complexes are at the red-sensitive limit of the spectrometer and made accurate correction difficult. In cases where corrected emission spectra were possible (all except dpq bimetallic complexes), a red shift of ~0.12 eV was observed in going from uncorrected to corrected spectra.

Excitation spectra were similar to the absorption spectra of the complexes in all cases. Emission quantum yields were not determined owing to a tailing of the emission peak past the limit of our detector.

Lifetime Measurements

Excited-state lifetimes were measured in acetonitrile solution of 25 °C. Excitation was accomplished using a Photochemical Research Associates LN 1000 Pulsed Nitrogen Laser/LN 107 Dye Laser System. The laser light was passed into the sample and viewed at right angles by a thermoelectrically cooled, Hamamatsu R928 detector in series with an Instruments, S.A. Model H-10 scanning monochromator. The signal was stored in a Stanford Research Systems SR 280 Boxcar averager that was triggered by a PRA Model L-OT trigger. The entire system was controlled by an IBM PC using software developed by Stanford Research Systems and modified in our laboratories. The lower limit of detectable lifetime for this configuration is ~2 ns and is limited by the rise time of the detector.

Electrochemistry

Cyclic voltammetry measurements were made with an IBM EC 225/3A, a Bioanalytical Systems CV-1B, or a PAR Model 273 electrochemistry system. Measurements were made at a sweep rate of 100 mV/s. Millimolar solutions of the Ru(II) complexes were prepared in acetonitrile with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. The solutions were deoxygenated by bubbling with N_2 gas. Measurements were made under a N_2 atmosphere at a Pt working electrode against a saturated calomel electrode. The measurements were uncorrected for junction potentials.

Results and Discussion

Electronic Absorption Spectra

The absorption spectra of the mono- and bimetallic phen complexes are given in Table 1 along with literature values from other studies. All complexes display intense metal-to-ligand charge-transfer (MLCT) absorptions in the visible region of the spectrum assigned as Ru $d_\pi \rightarrow$ polyazine p_{π^*} in nature. The internal ligand (π–π^*) transitions observed for Ru(II) polypyridine complexes [20, 21] are also observed for these systems [14, 20] but will not be discussed extensively. Reasonably high molecular symmetry is observed for the well-known, tris complexes $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ (D_{3d}). However, the other tris complexes, $Ru(dpp)_3^{2+}$ and $Ru(dpq)_3^{2+}$, will have a molecular symmetry that depends on whether the geometric isomers are facial (C_3) or meridinal (C_1). In the mixed-ligand monometallic and bimetallic complexes, there are no rigorous symmetry elements although treatment of the systems as ML_2L' would allow the complexes to approximate C_2 symmetry.

For the monometallic tris complexes, $Ru(bpy)_3^{2+}$, $Ru(phen)_3^{2+}$ and $Ru(dpp)_3^{2+}$, all have similar MLCT absorption features centered approximately at 450 nm with $Ru(phen)_3^{2+}$ having the added feature of a shoulder at 422 nm. The remaining tris species, $Ru(dpq)_3^{2+}$, is red-shifted to give a lower energy transition at 500 nm (499 nm in ref. 15b). The variety of peaks and shoulders make it difficult to assign all of the spectral features, however, qualitative similarity to $Ru(bpy)_3^{2+}$ would lead to analogous assignments.

The mixed-ligand monometallic species display two or three absorption maxima in the Ru $d_\pi \rightarrow$ ligand p_{π^*} wavelength region of the spectrum with the lowest energy absorption being slightly lower in energy than the corresponding tris dpp or dpq complexes. The lowest energy wavelength maximum for the dpp complexes appear at about 465 nm and at about 517 nm for the dpq complexes. This low energy MLCT transition is assigned to the Ru $d_\pi \rightarrow$ dpp [14] or $\rightarrow$ dpq [15a] p_{π^*} transition. A higher energy maximum is observed for $Ru(phen)_2dpq^{2+}$ at 434 nm compared to 441 nm for $Ru(bpy)_2dpq^{2+}$ [15b]. $Ru(phen)_2dpq^{2+}$ and $Ru(bpy)_2dpq^{2+}$ also possess relatively higher energy maxima at approximately 425 nm. These higher energy MLCT absorptions are assigned to the Ru $d_\pi \rightarrow$ phen or bpy p_{π^*} transitions. These assignments are consistent with the resonance Raman studies of Gafney and coworkers [14] with $Ru(bpy)_2dpp^{2+}$ and $[Ru(bpy)_2]_2dpp^{4+}$. The higher energy absorption bands observed for these complexes in the wavelength region of interest are 387 nm for $Ru(phen)_2dpp^{2+}$ and 350 nm for $Ru(phen)_2dpq^{2+}$ and $Ru(bpy)_2dpq^{2+}$. These absorptions are assigned to the polyazine ligand $p_\pi \rightarrow p_{\pi^*}$ transitions [14, 15].

Similar electronic spectra are found for the bimetallic complexes including the homo-ligand and mixed-ligand species within the respective set of dpp or dpq complexes. The lowest energy MLCT lies at approximately 525 nm for the dpp complexes and at approximately 603 nm for the dpq complexes. A shift to lower energy is observed in the absorption spectra in going from the monometallic mixed-ligand species to the bimetallic species. This lowest energy transition, as in the monometallic mixed-ligand species, is assigned to the Ru $d_\pi \rightarrow$ bridging ligand dpp or dpq p_{π^*} transition [14, 21].

Emission Spectra

In the case of the tris monometallic species (Table 1) the emission spectra show a ligand $p_{\pi^*} \rightarrow$ Ru d_π MLCT transition [12, 22]. The highest energy to lowest energy transitions follow this order: 585 nm for $Ru(phen)_3^{2+}$, 603 nm for $Ru(bpy)_3^{2+}$, 623 nm for $Ru(dpp)_3^{2+}$, and a large shift to lower energy for $Ru(dpq)_3^{2+}$ at 716 nm. These emission maxima parallel the lowest energy absorption maxima with energy differences between absorption and emission for $Ru(bpy)_3^{2+}$, $Ru(phen)_3^{2+}$, $Ru(dpp)_3^{2+}$ and $Ru(dpq)_3^{2+}$ of 0.69, 0.66, 0.73 and 0.74 eV, respectively.

TABLE 1. Absorption and emission spectroscopy and excited-state lifetimes of ruthenium/1,10-phenanthroline and related complexes[a]

Complex	Absorption		Emission	
	λ_{max} (nm)	$10^4 \times \epsilon_{max}$ (M^{-1} cm^{-1})	λ_{max} (nm)[b]	τ_m (ns)
$Ru(bpy)_3^{2+}$[c]	450	1.38	603	850
$Ru(phen)_3^{2+}$[c]	447	1.84	585	500
$Ru(dpp)_3^{2+}$	455	1.54	623	183
	455[d]	1.65	636	270
$Ru(dpq)_3^{2+}$	500	1.51	716	82
	499[e]	1.4	714[f]	70
$Ru(phen)_2dpp^{2+}$	465(sh)	1.06	652	252
	434	1.39		
$Ru(bpy)_2dpp^{2+}$	464(sh)	1.15	660	226
	441	1.19		
	470(sh)[g]		675	135
	430	1.2		
$Ru(phen)_2dpq^{2+}$	516	1.10	756	83
	422(sh)	1.15		
	351(sh)	1.86		
$Ru(bpy)_2dpq^{2+}$[e]	517	0.84 (0.94)[h]	760	$\leqslant$20
	426(sh)	0.87 (0.87)[h]	(766)[h]	(71)[h]
	391(sh)			
	350(sh)	(1.67)[h]		
$[Ru(phen)_2]_2(dpp)^{4+}$	525	2.34	746	153
	423	2.10		
	364(sh)	2.49		
$[Ru(bpy)_2]_2(dpp)^{4+}$	523	2.25	756	134
	426	1.98		
	525[g]	2.1	755	54
	425	1.7		
$(phen)_2Ru(dpp)Ru(bpy)_2^{4+}$	523	2.74	752	113
	425	2.35		
$[Ru(phen)_2]_2(dpq)^{4+}$	601	2.20	810	20
	420(sh)			
	398	3.09		
	380(sh)	3.08		
$[Ru(bpy)_2]_2(dpq)^{4+}$	603	1.82	822	<20
	420(sh)			
	399	2.34		
	380(sh)	1.96		
	605	0.98		
	423(sh)			
	399	1.2		
	382(sh)			
$(phen)_2Ru(dpq)Ru(bpy)_2^{4+}$	603	2.54	820	<20
	420(sh)			
	398	3.25		
	381(sh)	2.96		

[a] In acetonitrile at 25 °C unless noted. [b] Uncorrected for detector response. [c] Ref. 19. [d] In H_2O, ref. 12. [e] Ref. 15b. [f] In 4:1 EtOH/MeOH. [g] In H_2O, ref. 14. [h] This work. [i] In H_2O, ref. 15a.

The mixed-ligand monometallic species also display one emission band which is assigned to the dpp [14] or dpq $p_{\pi^*} \rightarrow$ Ru d_π transition. Similar wavelengths of emission exist between the two groups of complexes, dpp or dpq ligand containing. $Ru(phen)_2dpp^{2+}$ displays an emission at 652 nm similar to the 660 nm reported for $Ru(bpy)_2dpp^{2+}$ [14]. The emission of the dpq complex shifts to longer wavelengths with $Ru(phen)_2dpq^{2+}$ giving an emission of 756 nm compared to 766 nm for the bpy analog [15b]. Again, the emission maxima parallel the lowest absorption maxima with energy differences between the absorption and emission for $Ru(phen)_2dpp^{2+}$, $Ru(bpy)_2dpp^{2+}$, $Ru(phen)_2dpq^{2+}$ and $Ru(bpy)_2dpq^{2+}$ of 0.77, 0.79, 0.67 and 0.68 eV, respectively. Not only are the shifts from absorption to emission maxima relatively constant for the mixed-ligand monometallic complexes, but they are very similar to the tris complexes. This parallelism, in conjunction with previous resonance Raman studies, indicates that the emissive excited state (at least in the mixed-ligand complexes) is localized within the chelate ligand that has the lowest energy π^* orbital (dpp or dpq in this study).

The bimetallic complexes also show a MLCT emission assigned as a dpp [14] or dpq $p_{\pi^*} \rightarrow$ Ru d_π transition. The bimetallic species again show the same type of transition as seen in the mixed-ligand monometallic species with similar emission bands among the complexes of that particular dpp or dpq group. The dpp complexes show emissions ranging from 756 to 746 nm, while again the dpq complexes are shifted to longer wavelengths ranging from 822 to 810 nm. The emission maximum parallels the lowest energy absorption maxima with energy differences between absorption and emission for $[Ru(phen)_2]_2phen^{4+}$, $[Ru(bpy)_2]_2dpp^{4+}$, $(phen)_2Ru(dpp)Ru(bpy)_2^{4+}$, $[Ru(phen)_2]_2dpq^{4+}$, $[Ru(bpy)_2]_2dpq^{4+}$ and $(phen)_2Ru(dpq)Ru(bpy)_2^{4+}$ of 0.69, 0.73, 0.72, 0.53, 0.55 and 0.55 eV, respectively. The dpp bridged systems have approximately the same absorption/emission shift as observed for the mixed-ligand and tris monometallic complexes. This result, which will be further reinforced by the electrochemistry data later in this section supports a localized excited state involving the π^* LUMO of the bridging dpp. The dpq bridged systems, while showing consistent absorption/emission shifts within themselves, have slightly smaller shifts than all of the other complexes in this study. While this difference may be due to a different excited-state distortion or the mixing of the emitting state with a lower energy, non-spectroscopic state, it might also be an artifact due to the difficulty in measuring emission spectra for phototube response at wavelengths longer than 800 nm.

Electrochemistry

The results of the cyclic voltammetric measurements for the metal oxidations and bound ligand reductions are summarized in Table 2. The $E_{1/2}$ values were determined by averaging the anodic and cathodic peak potentials for the oxidation and reduction waves, respectively. The values in parentheses correspond to ΔE_p, the difference in the cathodic and anodic peak potentials in millivolts.

The Ru(II) tris species show one reversible oxidation, Ru(II) → Ru(III) [12, 23]. While similar oxida-

TABLE 2. Electrochemistry of mono- and bimetallic ruthenium/phenanthroline and related complexes[a]

Complex	Oxidations[b]			Reductions[c]		
	$E_{1/2}(1)^{ox}$	$E_{1/2}(2)^{ox}$	K_{com}[d]	$E_{1/2}(1)^{red}$	$E_{1/2}(2)^{red}$	$E_{1/2}(3)^{red}$
$Ru(bpy)_3^{2+}$[e]	1.26(68)			−1.35(65)	−1.53(70)	−1.78(79)
$Ru(phen)_3^{2+}$	1.31(80)			−1.34(85)	−1.47(85)	
	1.40[f]			−1.41	−1.54	−1.84
$Ru(dpp)_3^{2+}$[g]	1.68			−0.95	−1.12	−1.39
$Ru(dpq)_3^{2+}$	1.65(80)			−0.62(60)	−0.80(75)	−1.06(70)
	1.70[h]			−0.60	−0.78	−1.04
$Ru(phen)_2dpp^{2+}$	1.39(80)			−1.07(85)	−1.35(285)	
$Ru(bpy)_2dpp^{2+}$	1.33(75)			−1.06(80)	−1.48(90)	
	1.31[g]			−1.06	−1.50	
$Ru(phen)_2dpq^{2+}$	1.42(90)			−0.79(85)	−1.50(295)	
$[Ru(phen)_2]_2(dpp)^{4+}$[i]	1.41(58)			−0.78(64)	−1.41(75)	
$[Ru(bpy)_2]_2(dpp)^{4+}$	1.44(110)	1.65(100)	3.6×10^3	−0.64(70)	−1.13(70)	−1.4(200)
$[Ru(bpy)_2](dpp)^{4+}$[j]	1.30	1.49		−0.64		
	1.38(70)	1.56(95)	1.1×10^3	−0.66(85)	−1.14(85)	
$(phen)_2Ru(dpp)Ru(bpy)_2^{4+}$	1.41(65)	1.61(70)	2.4×10^3	−0.6(k)	−1.15(k)	−1.4(k)
$[Ru(bpy)_2]_2(dpq)^{4+}$	1.48(60)	1.64(60)	5.1×10^2	−0.40(60)	−1.09(60)	−1.4(145)
$[Ru(phen)_2]_2(dpq)^{4+}$[i]	1.47(72)	1.62(61)	3.4×10^3	−0.37(58)	−1.10(72)	
$(phen)_2Ru(dpq)Ru(bpy)_2^{4+}$	1.51(85)	1.69(90)	1.1×10^3	−0.36(70)	−1.08(60)	−1.41(160)

[a] Recorded in acetonitrile at 25 °C with 0.1 M TBAP as supporting electrolyte. Potentials are reported in volts vs. SCE with anodic/cathodic peak-to-peak separations in parenthesis in mV. $E_{1/2}$ values are the average of the anodic and cathodic peaks. [b] $E_{1/2}(1)^{ox}$ corresponds to Ru(III)/Ru(II) or Ru(III, II)/Ru(II, II) couples; $E_{1/2}(2)^{ox}$ corresponds to Ru(III, III)/Ru(III, II) couple. [c] $E_{1/2}{}^{red}$ represents the successive ligand based reductions. [d] Comproportionation constant, M^{-1}, calculated from $E_{1/2}(1)^{ox}$ and $E_{1/2}(2)^{ox}$. [e] Ref. 23. [f] Ref. 24. [g] Ref. 12. [h] Ref. 15b. [i] Ref. 15a. [j] Ref. 14b. [k] Indicates the position of the cathodic wave in systems which display chemical as well as electrochemical irreversibility.

tion potentials result for the pair of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$, the pair of $Ru(dpp)_3^{2+}$ and $Ru(dpq)_3^{2+}$ have similar potentials to each other but are more difficult to oxidize than the former pair by 0.40 V. The reversible reductions of the ligands of these complexes again show similar potentials for the Ru(II) tris-chelated bpy and phen compounds but differing potentials for the dpp and dpq complexes. $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ are the most difficult to reduce of the four complexes being discussed, followed by $Ru(dpp)_3^{2+}$ which is less difficult to reduce and finally, $Ru(dpq)_3^{2+}$ which is the easiest to reduce. ΔE_p values for the complexes, which are chemically (and sometimes electrochemically) reversible, range from 60–85 mV.

The energy difference between the first oxidation and the first reduction of the tris complexes (Table 2) parallels the absorption/emission energy difference. In all cases the $E_{1/2}(1)^{ox} - E_{1/2}(1)^{red}$ value calculated from Table 2 is 0.1–0.2 eV less than the absorption energy and 0.5–0.6 eV more than the emission energy. This difference in potential represents the thermodynamic difference between $Ru(II)L_3^{2+}$, and the combination $Ru(III)L_3^{3+}$ and $Ru(II)(L_3)^+$ which mimics the MLCT ground-state/excited-state energy difference. Thus, all of the data are consistent with the MLCT nature of the excited state although there is still some controversy over whether the initial excited state formed is localized with one L [5, 25] or delocalized over all three L [26], especially in non-polar solvents or the solid state [26b].

The monometallic mixed-ligand complexes display one-electron, quasi-reversible oxidations with potentials that are similar for the dpp complexes and the dpq complexes, with the dpq systems slightly more difficult to oxidize (Table 2). Two or three reduction waves are observed for each of these complexes which are assigned to the ligand reductions. The first reduction for the dpq mixed-ligand complexes occurs ~0.30 V less negative than the analogous reduction for the dpp mixed-ligand complexes. The second reductions are similar for all four monometallic compounds with only a 0.15 V difference from lowest to highest potential and are assigned to reduction of phen or bpy. Chemically reversible waves are observed for most of these reductions with ΔE_p ranging from 65–85 mV. Some selected phen reductions are in the $\Delta E_p \simeq 300$ mV range as a consequence of adsorption of the reduced phen complex onto the electrode surface.

As substitution on the tris complex is made to form the mixed-ligand RuL_2L' species, different behavior is observed for the potentials of the oxidations and the various reductions. The reductions are very ligand specific as has been discussed for $Ru(bpy)_3^{2+}$, $Ru(bpy)_2dpp^{2+}$ and $Ru(dpp)_3^{2+}$ in a previous paper [13]. The first oxidation, on the other hand, appears to depend on the average ligand environment at the Ru(II) center. In addition, as was the case in the tris, symmetrical complexes, the difference in energy between the first oxidation and the first reduction parallels the absorption and emission maxima in an analogous manner. Thus, it is not only the nature of the ligand with the lowest-energy π^* orbital that determines the excited-state energy in these ruthenium systems, but also the average ligand environment which can be used to fine tune the energy. This variation in excited-state donor energy and variety in ground- and excited-state redox potentials gives these systems great flexibility for excited-state energy- or electron-transfer processes.

Bimetallic Complexes

For the bimetallic complexes, the two oxidations in Table 2 correspond to the following

$$\text{Ru(II),Ru(II)} \xrightarrow{E_{1/2}(1)^{ox}} \text{Ru(II),Ru(III)} \xrightarrow{E_{1/2}(2)^{ox}} \text{Ru(III),Ru(III)}$$

Oxidations are comparable between the two bridging ligand groups of bimetallic species with the dpq complexes being slightly more difficult to oxidize than the dpp complexes, as seen in the monometallic species. The ΔE_p values range from 60–110 mV for these oxidations. Again two to three reductions are seen for each of these complexes; although, the ligand reductions have shifted to more positive potentials than their corresponding monometallic counterparts. The ΔE_p values range from 60–200 mV, with the larger separation attributed to slow electron transfer and adsorption of the complexes onto the electrode surface.

The comproportionation constant, K_{com} (Table 2), was calculated for the bimetallic species from the electrochemical data. K_{com} is given by

$$[\text{Ru(II)Ru(II)}] + [\text{Ru(III)Ru(III)}] \overset{K_{com}}{\rightleftharpoons} 2[\text{Ru(II)Ru(III)}]$$

$$K_{com} = \frac{[\text{Ru(II)Ru(III)}]^2}{[\text{Ru(II)Ru(II)}]\,[\text{Ru(III)Ru(III)}]}$$

$$K_{com} = \exp[E_{1/2}/25.69]$$

in which the stability of the [Ru(II)Ru(III)] complex is assessed. The statistical value for these bimetallic systems is 4 [27]. The values for the dpp complexes are approximately 10^3 while the dpq complexes are in the order of 10^2. As was the case in the monometallic systems, the reductions appear to be associated with specific ligands while the oxidations reflect the average ligand environment at the ruthenium center.

Excited State Lifetimes

Lifetimes for the mono- and bimetallic complexes were measured under identical conditions as for the emission spectra. The values are displayed in the last column of Table 2. Long lifetimes [28] are observed for the symmetrical $Ru(bpy)_3^{2+}$ at 850 ns and $Ru(phen)_3^{2+}$ at 500 ns. $Ru(dpp)_3^{2+}$ shows a shorter lifetime at 183 ns [13] and $Ru(dpq)_3^{2+}$ shows an even shorter lifetime of 82 ns. The lifetimes for the unsymmetrical monometallic species show comparable lifetimes among groups. $Ru(bpy)_2dpp^{2+}$ and $Ru(phen)_2dpp^{2+}$ display lifetimes of 226 and 252 ns, respectively. The dpq complexes give shorter lifetimes of 71 ns for $Ru(bpy)_2dpq^{2+}$ and 83 ns for $Ru(phen)_2dpp^{2+}$.

The bimetallic complexes also show comparable emission lifetimes among groups of dpp and dpq bridged systems. The dpp complexes show lifetimes of 134 ns for $[Ru(bpy)_2]_2dpp^{4+}$, 153 ns for $[Ru(phen)_2]_2dpp^{4+}$ and 113 ns for $(phen)_2Ru(dpp)Ru(bpy)_2^{4+}$. Only one dpq complex has a measurable emission lifetime, $[Ru(phen)_2]_2(dpq)^{4+}$, which has a lifetime of 20 ns. (It is presumed that the remaining two dpq complexes have lifetimes of less than 20 ns since this would be in accordance with the dpp bimetallic lifetime trend; although, values of less than 20 ns could not be accurately measured with the available instrumentation.)

Metal–Metal Communication

The emission of these bimetallic complexes at room temperature in fluid solution is novel to ruthenium chemistry and has been attributed to lack of coupling between the metal centers when bridged by dpp or dpq [14]. The major data used in these arguments are the electrochemistry of the mono- and bimetallic complexes. When the difference in the first oxidation between the mono- and bimetallic complex is small (e.g. 0.05 V for $Ru(bpy)_2dpp^{2+}$ and $[Ru(bpy)_2]_2dpp^{4+}$), emission is observed in the bimetallic complex [14]. However, when the difference in first oxidation potentials is large (e.g. 0.17 V for $Ru(bpy)_2bpm^{2+}$ and $[Ru(bpy)_2]_2bpm^{4+}$ (bpm = 2,2′-bipyrimidine)) [14b], no room temperature emission is observed for the bimetallic complex. Our results are compatible with this interpretation in that all six bimetallic complexes using dpp or dpq as a bridging ligand show $\Delta E_{1/2} \leqslant 0.06$ V between mono- and bimetallic species and a room temperature emission [15, 29]. In addition, recent work in our laboratories [19] involving tetrametallic complexes centered around $Ru(dpp)_3^{2+}$ and dpp bridged Fe–Ru bimetallic complexes [30] also show room temperature emission consistent with this interpretation. At this time our conclusion is that while the large comproportionation constant reflects a net stability of the mixed-valence species (II,III) over the isovalent complexes (II,II and III,III), electrochemical and emission data suggest that metal–metal interaction in the isovalent (II,II) complex is small with dpp and dpq bridging ligands.

In addition, the combination of excited-state energies which are dependent on the ligand with the lowest energy π^* level, and ground-state oxidations which depend on the average ligand environment at the metal, and reductions which are ligand specific for the series of mono-, bi- and tetrametallic complexes [31] results in a system where a variety of excited-state energies are not necessarily coupled to the excited-state, oxidation/reduction energies. As a consequence, these systems may be very important in studying competitive energy- and electron-transfer processes.

Supplementary Material

Elemental analyses for the new compounds are available from the authors on request.

Acknowledgements

Acknowledgement is made to the Office of Basic Energy Research, Department of Energy (DE-AS09-80ER10671 and DE-FG09-87ER13768) for support of the research, to the South Carolina Energy Research and Development Center for portions of the instrumentation, and to Johnson-Matthey, Inc. for donating the ruthenium used in these studies. Dr John D. Petersen also acknowledges an Alexander von Humboldt Research Fellowship at the Universität Regensburg during the preparation of this manuscript.

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