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Excited State Properties of Mixed Phosphine 2-(2′-Pyridyl)quinoline Complexes of Ruthenium(II)

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Mixed ligand complexes of the type $Ru(pq)_2(PP)^{2+}$ (pq = 2,2′-pyridylquinoline and PP = one bidentate or two monodentate phosphine ligands) have been prepared from the appropriate phosphine and $Ru(pq)_2Cl_2$. The room temperature absorption spectra and low temperature (77 K) emission spectra, emission lifetimes, and quantum yields have been measured for the series of complexes and compared with those of $Ru(pq)_3^{2+}$ and analogous $Ru(bpy)_2(PP)^{2+}$ complexes (bpy = 2,2′-bipyridine) where possible. Emission spectra have been fit using a single mode Franck–Condon analysis. The visible absorption bands and emission bands are assigned to MLCT transitions that are blue shifted relative to $Ru(pq)_3^{2+}$, while the emission lifetimes and quantum yields are increased. The trends in the nonradiative rate constants, k_{nr}, are described in terms of the energy gap, E_0, and the Huang–Rhys factor, S_M, which were obtained from the spectral fittings, and are correlated with the phosphine ligand structures.

Since the first report[1] of emission by $[Ru(bpy)_3]^{2+}$ (bpy is 2,2′-bipyridine), a tremendous amount of research has been done to characterize the nature of the electronic excited states in polypyridyl complexes of ruthenium.[2−10] The properties of these excited states can be varied systematically by changing the ligands. This may be accomplished by using bidentate or polydentate rings and cages with different structures[11,12] or by changing the number and location of single substituents or benzo groups attached to the polypyridine ligand.[13−19] The number of compounds studied has increased substantially by the synthesis of mixed ligand complexes with symmetrical and asymmetrical diimine ligands[20−33] or with ligands that coordinate to ruthenium(II)

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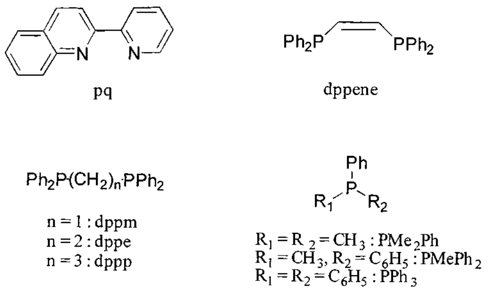

Figure 1. Ligand structures. Abbreviations: pq = 2-(2′-pyridyl)quinoline; dppene = *cis*-bis(diphenylphosphino)ethylene; dppm = 1,2-bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; PMe_2Ph = dimethylphenylphosphine; $PMePh_2$ = methyldiphenylphosphine; PPh_3 = triphenylphosphine.

through elements other than nitrogen (C, P, O, S, halogens, etc.).[34−39] The focus of our research has been the study of complexes with bipyridine or phenanthroline ligands with substituents in sterically hindering positions.[13,14,20] In this paper, we report the synthesis and photophysical properties of a series of ruthenium(II) mixed ligand complexes, $[Ru(pq)_2(PP)]^{2+}$, which contain one bidentate or two monodentate phosphine ligands (PP), where PP = *cis*-$Ph_2PCH{=}CHPPh_2$, $Ph_2P(CH_2)_nPPh_2$ with $n = 1$, 2, or 3, or PP = $(PMe_2Ph)_2$, $(PMePh_2)_2$, or $(PPh_3)_2$, in addition to two sterically hindering benzo substituted bipyridine ligands, pq, (where pq = 2-(2′-pyridyl)quinoline). The structures of these ligands are shown in Figure 1.

The photophysical properties of polypyridine Ru(II) complexes are governed by ligand $\pi\pi^*$ states, metal-to-ligand charge-transfer, MLCT, states, and metal centered dd states. We have been interested in complexes with pq because the additional electron delocalization in this ligand, compared to bpy, changes the energy of both the $\pi\pi^*$ and MLCT states. Furthermore, the position of the additional ring in pq causes steric hindrance around the metal center, which alters the position of the dd states. Also of interest is the influence that phosphine ligands, with their back-bonding ability and steric crowding, have on the excited states and the resulting photophysical properties. The effect on the MLCT states is of particular interest because the pq ligand, compared to bpy, causes a red shift in the MLCT absorption and emission bands, a shortening of the emission lifetime, and a smaller quantum yield.[7] In contrast, when phosphine ligands replace a bpy ligand, it causes a blue shift in both the MLCT absorption[34] and emission[35] bands. For osmium complexes at room temperature in acetonitrile, phosphine ligands produce a longer emission lifetime and an increased quantum yield.[40] That is, the pq and phosphine ligands have opposite effects on the photophysical properties of complexes that contain them. The results are of significance for what they reveal about the combined effects of pq and phosphine ligands on excited-state properties of ruthenium polypyridine complexes.

Experimental Section

Materials. $RuCl_3$ was obtained from Engelhard Industries, all phosphine ligands were obtained from Strem Chemical Co., and all were used without further purification. 2-(2′-Pyridyl)quinoline (pq) was prepared by literature methods.[41] All the chemicals used in the syntheses were reagent grade, and spectrophotometric grade solvents were used as received for spectroscopic measurements. Elemental analyses were performed by Galbraith Laboratories, Inc.

Preparations. ***cis*-$[Ru(pq)_2Cl_2]\cdot 2H_2O$.** The preparation of this compound is a modification of the procedure developed by Sullivan et al.[34] for the analogous bipyridine complex. Commercial $RuCl_3\cdot 3H_2O$ (1.95 g, 7.46 mmol), pyridylquinoline (3.09 g, 15.0 mmol), and LiCl (2.1 g, 0.50 mmol) in reagent grade dimethylformamide (12.5 mL) were heated under nitrogen at reflux for 12 h. After cooling to room temperature, 63 mL of reagent grade acetone was added and the resultant solution cooled at 0 °C overnight. The acetone was decanted through a fritted glass crucible and the residue washed onto the crucible with six 6-mL portions of water, producing a reddish-brown filtrate and a powdery dark purple solid. The solid was washed three times with 6-mL portions of diethyl ether and oven dried for 2 h at 50 °C. Yields ranged from 75% to 90% based on starting ruthenium.

Preparation of Monodentate Phosphine Complexes, *cis*-$[Ru(pq)_2(P)_2](PF_6)_2$ (P = PMe_2Ph, $PMePh_2$, PPh_3). This procedure is also a modification of that used by Sullivan et al.[34] In a typical preparation, *cis*-$Ru(pq)_2Cl_2\cdot 2H_2O$ (312 mg, 0.50 mmol) was suspended in 50 mL of a 1:1 water−ethanol solution (by volume), and a 100% excess of the phosphine ligand was added. With the $PMePh_2$ and PMe_2Ph ligands, the addition was performed in a N_2 filled glovebag. The mixture was deaerated with N_2 for ∼20 min using a Pasteur pipet and stirred vigorously with a magnetic stirrer while being heated at reflux under a N_2 atmosphere for 10−12 h. After the reflux period, the dark purple solution was evaporated in a stream of N_2 while heating continued until the volume was reduced by two-thirds. The mixture was then cooled, 10 mL of water added, and the unreacted ligand slowly filtered off as the solid tended to clog the filter. An excess of NH_4PF_6 in water was added to the purple or orange-red filtrate, and the solid product collected by filtration, washed three times with 6-mL portions of water and then three times with 6-mL portions of ether. The purple or reddish-purple solid was dissolved in 3 mL of acetonitrile and diluted with 7 mL of benzene followed by elution on a 1.5 cm × 20 cm column of alumina; the eluent was also benzene−acetonitrile (7:3 by volume). One or two purple bands eluted first, followed by a yellow or yellow-orange main band. The solutions were left overnight to evaporate the solvent. Final purification was achieved by dissolving the precipitate in a minimum amount of acetone and filtering, followed by slow addition of ether to the filtrate. The complexes were dried by suction. Yields ranged from 5% to 14% based on ruthenium.

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***cis*-[Ru(pq)$_2$(PMe$_2$Ph)$_2$](PF$_6$)$_2$·3H$_2$O.** After 10 h of refluxing, the complex was isolated and purified to produce reddish-brown crystals (28.4 mg, 5.0%). Anal. Calcd for $C_{44}H_{42}F_{12}N_4P_4Ru\cdot 3H_2O$: C, 46.61; H, 4.27; N, 4.94. Found: C, 46.25; H, 4.31; N, 5.23.

***cis*-[Ru(pq)$_2$(PMePh$_2$)$_2$](PF$_6$)$_2$.** After 10 h of refluxing, the complex was isolated and purified to produce reddish-brown crystals (86.9 mg, 14%). Anal. Calcd for $C_{54}H_{46}F_{12}N_4P_4Ru$: C, 53.88; H, 3.85; N, 4.65. Found: C, 54.21; H, 4.30; N, 5.36.

***cis*-[Ru(pq)$_2$(PPh$_3$)$_2$](PF$_6$)$_2$·3H$_2$O.** After 12 h of refluxing, the complex was isolated and purified to produce yellow-brown crystals (34.8 mg, 5.0%). Anal. Calcd for $C_{64}H_{50}F_{12}N_4P_4Ru\cdot 3H_2O$: C, 55.66; H, 4.09; N, 4.06. Found: C, 55.08; H, 3.89; N, 4.34.

Preparation of Bidentate Phosphine Complexes, [Ru(pq)$_2$(PP)](PF$_6$)$_2$ (PP = dppm, dppe, dppp, dppene). Basically, the same procedure described previously was used here. To improve yields, 1-propanol was substituted for ethanol to produce a higher reaction temperature, and longer reaction times were used. *cis*-Ru(pq)$_2$Cl$_2$·2H$_2$O (156 mg, 0.25 mmol) was suspended in 20 mL of a 1:1 water−1-propanol solution (by volume), and a 50%−70% excess of the phosphine ligand was added. The mixture was deaerated, stirred vigorously with a magnetic stirrer, and heated at reflux under a N_2 atmosphere for 9−16 h. After reflux, the volume was reduced by two-thirds and the mixture cooled overnight at 0 °C. The unreacted ligand was filtered off and an excess of NH_4PF_6 in water added to the reddish-brown filtrate. The solid product was collected and washed with water and ether. The brownish-yellow solid was chromatographed on alumina, eluting with benzene−acetonitrile. A light yellow band eluted first, followed by a light purple band. The end of the purple band overlapped the leading edge of the main yellow band which followed. After ∼50−100 mL of the main band was collected, the eluent concentration was changed to 50:50 to speed up the movement of the complex. Several brownish-red bands remained near the top. After recrystallization from acetone−ether, the complexes were obtained as brown to orange solids in 11%−31% yield.

[Ru(pq)$_2$(Ph$_2$PCH$_2$PPh$_2$)](PF$_6$)$_2$. After 9 h of refluxing, the dppm complex was isolated and purified to produce reddish-brown crystals (33.45 mg, 11.3%). Anal. Calcd for $C_{53}H_{42}F_{12}N_4P_4Ru$: C, 53.59; H, 3.56; N, 4.72. Found: C, 53.23; H, 3.71; N, 4.41.

[Ru(pq)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)](PF$_6$)$_2$. After 16 h of refluxing, the dppe complex was isolated and purified to produce brown-orange crystals (89.9 mg, 29.9%). Anal. Calcd for $C_{54}H_{44}F_{12}N_4P_4Ru$: C, 53.96; H, 3.69; N, 4.66. Found: C, 54.04; H, 3.92; N, 4.42.

[Ru(pq)$_2$(Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$)](PF$_6$)$_2$·H$_2$O. After 12 h of refluxing, the dppp complex was isolated and purified to produce orange crystals (41.5 mg, 13.5%). Anal. Calcd for $C_{55}H_{46}F_{12}N_4P_4Ru\cdot H_2O$: C, 53.54; H, 3.92; N, 4.54. Found: C, 53.38; H, 3.91; N, 4.39.

[Ru(pq)$_2$(*cis*-Ph$_2$PCH=CHPPh$_2$)](PF$_6$)$_2$. After 12 h of refluxing, the dppene complex was isolated and purified to produce brown-orange crystals (92.9 mg, 31.0%). Anal. Calcd for $C_{54}H_{42}F_{12}N_4P_4Ru$: C, 54.05; H, 3.53; N, 4.67. Found: C, 53.75; H, 3.74; N, 4.50.

Spectroscopic Measurements. Absorption spectra were measured in methanol at room temperature in 1-cm quartz cells using a Beckman DU 7400 diode array spectrophotometer. Each spectrum corresponds to a signal average of 20 individual spectra collected at 0.1-s intervals. Absorption maxima are accurate to ±2 nm. Molar absorptivity values were determined by measuring the absorbance at three or more different concentrations.

Emission spectra were recorded with an American Instrument Co. Aminco-Bowman spectrophotofluorometer previously described.[42] All luminescence spectra, quantum yields, and lifetimes were measured at 77 K in ethanol−methanol (4:1 v/v) rigid glasses as previously reported for other complexes.[14] Relative uncertainty in the emissiom maxima, lifetime measurement, and quantum yield, reported as 2σ, does not exceed 2%, 8%, and 14%, respectively. No evidence of dissociation or photodecomposition of the complexes was observed during the measurements.

Emission Spectral Fitting. The spectra were fit by a single mode Franck−Condon analysis from the equation developed by Meyer and co-workers.[11,24,35,40,43−45]

$$I(E) = \sum_{\upsilon_M=0}^{10}\left\{\left(\frac{E_0-\upsilon_M\hbar\omega_M}{E_0}\right)^3\left(\frac{S_M^{\upsilon_M}}{\upsilon_M!}\right)\exp\left[-4\ln(2)\left(\frac{E-E_0+\upsilon_M\hbar\omega_M}{\Delta\nu_{1/2}}\right)^2\right]\right\}$$

$I(E)$ is the intensity of emission at energy E in reciprocal centimeters relative to the emitted intensity at the maximum, υ_M are the vibrational quantum numbers for the medium frequency ($\hbar\omega_M$) ligand acceptor modes, E_0 is the energy gap between the ground and excited emitting state, S_M is the electron-vibrational coupling constant or Huang−Rhys factor, and $\Delta\nu_{1/2}$ is the full width at half-maximum of the zeroth-order vibronic transition. The fitting of the spectrum was accomplished by digitizing the measured emission spectrum (typically 50 points) and converting it to an abscissa linear in energy and normalized so that $I_{max} = 100$. After selecting the initial parameters,[43] the spectrum was calculated and compared to the experimental points. The parameters were varied until a good fit was attained.

Results and Discussion

Syntheses. The complex *cis*-[Ru(pq)$_2$Cl$_2$] was produced in fairly high yields from RuCl$_3$ and pq by refluxing in DMF with excess LiCl. The synthesis of the [Ru(pq)$_2$(PP)](PF$_6$)$_2$ complexes was accomplished in a straightforward manner by displacement of Cl from Ru(pq)$_2$Cl$_2$ in ethanol− or propanol−water solution, following essentially the same procedures used for analogous ruthenium bipyridine complexes. The much lower yields, despite longer reflux times, are not surprising considering the sterically hindering nature of pyridylquinoline compared to bipyridine and the steric requirements of the phosphine ligands. The stabilizing effect of the chelating phosphine ligands and a higher reaction temperature produced higher yields than those obtained for the monodentate ligands. Purification of the complexes was accomplished by column chromatography on alumina using the colors of the complexes to separate the components of the reaction mixture. The purified compounds gave satisfactory elemental analyses.

Electronic Absorption Spectra. The ultraviolet and visible absorption data are given in Table 1. Figure 2 shows the absorption spectra in the ultraviolet region of two phosphine pyridylquinoline complexes as well as the spectrum of the free pyridylquinoline ligand. The bands in the UV arise from pq-based $\pi \rightarrow \pi^*$ transitions, and the similarity among the different Ru complexes and their

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Table 1. Absorption Data for $Ru^{II}(pq)_2(PP)_2^{2+}$ and $Ru^{II}(pq)_3^{2+}$ Complexes in MeOH Solution[a]

	λ_{max} (nm) ($\epsilon \times 10^{-3}$ (M^{-1} cm^{-1}))					
$[Ru(pq)_2(Ph_2PCH_2PPh_2)](PF_6)_2$	228 (70.6)	269 (36.2)	294 sh (25.4)	338 (17.0)	355 (15.8)	417 (5.8)
$[Ru(pq)_2(Ph_2P(CH_2)_2PPh_2)](PF_6)_2$	228 (68.4)	269 (35.0)	295 sh (23.0)	339 (16.6)	356 (16.6)	420 (6.1)
$[Ru(pq)_2(Ph_2P(CH_2)_3PPh_2)](PF_6)_2$	228 sh (64.4)	273 (32.5)	296 sh (24.6)	342 (16.1)	358 (16.2)	432 (6.1)
$[Ru(pq)_2(\textit{cis}\text{-}Ph_2PCH{=}CHPPh_2)](PF_6)_2$	224 (68.5)	269 (33.8)		340 (16.7)	356 (18.1)	408 (5.5)
$\textit{cis}\text{-}[Ru(pq)_2(PMe_2Ph)_2](PF_6)_2$	244 sh (37.4)	273 (27.7)	309 (22.6)	339 sh (13.9)	356 (11.2)	442 (4.2)
$\textit{cis}\text{-}[Ru(pq)_2(PMePh_2)_2](PF_6)_2$	244 sh (44.7)	273 (36.4)	312 (27.2)	339 sh (17.9)	356 (12.6)	440 (5.5)
$\textit{cis}\text{-}[Ru(pq)_2(PPh_3)_2](PF_6)_2$	246 (52.8)	274 (43.3)	312 (35.5)	340 sh (22.9)	356 (15.2)	445 (7.0)
$[Ru(pq)_3](ClO_4)_2$	248 (54.4)	273 (62.1)	311 (52.1)			484 (13.4)

[a] λ_{max} ± 2 nm; $T = 298$ K.

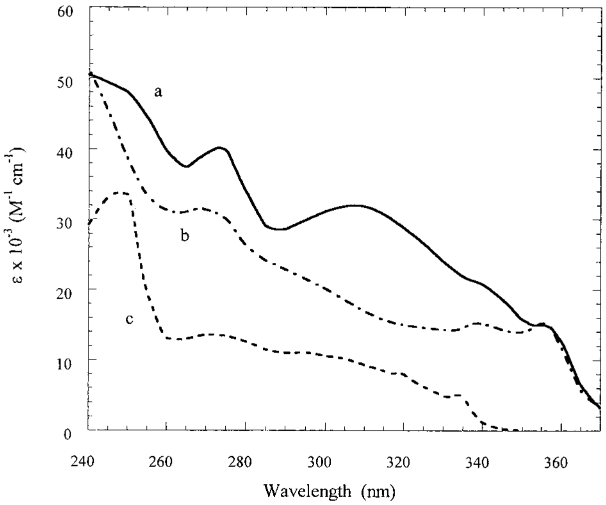

Figure 2. Ultraviolet absorption spectra in methanol solution at room temperature of (a) $Ru(pq)_2(PPh_3)_2^{2+}$, (b) $Ru(pq)_2(dppe)^{2+}$, and (c) pq ligand.

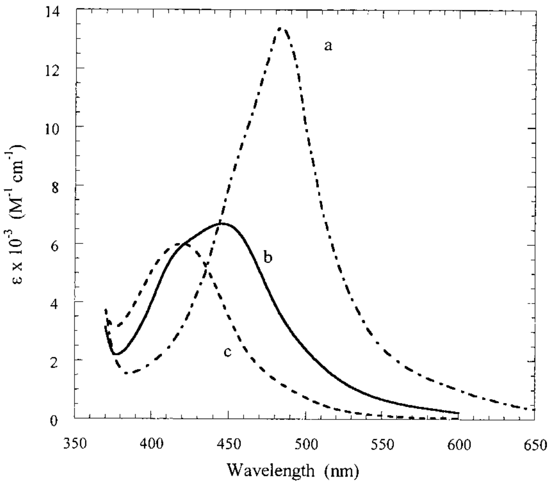

Figure 3. Visible absorption spectra in methanol solution at room temperature of (a) $Ru(pq)_3^{2+}$, (b) $Ru(pq)_2(PPh_3)_2^{2+}$, and (c) $Ru(pq)_2(dppe)^{2+}$.

similarity with the free pq ligand absorptions, for example at 246, 274, and 312 nm for $[Ru(pq)_2(PPh_3)_2]^{2+}$, is apparent. The two bands in the pq spectrum at 319 and 334 nm (31 350 and 29 940 cm^{-1}) appear in the spectra of the complexes, but red shifted to 339 and 356 nm (29 500 and 28 090 cm^{-1}), yet maintaining about the same energy difference (1400 cm^{-1}), indicative of a ligand vibrational mode. The differences in the values of the molar absorptivity, ϵ, for the different ruthenium complexes is not great, but, except for the band at 248 nm, the greater number of pq moieties in the complexes produces more intense bands than those observed for the free pq ligand. The $\pi \rightarrow \pi^*$ transitions for the phenyl rings on the phosphine ligands are expected to occur between 251 and 261 nm and are not discernible under the strong pq absorption at 247 nm.

Figure 3 shows the room-temperature visible absorption spectra of two representative phosphine complexes along with that of $Ru(pq)_3^{2+}$ for comparison. The bands in the visible can be assigned to $d\pi(Ru) \rightarrow \pi^*(pq)$ metal-to-ligand charge transfer (MLCT) transitions, as has been well established for complexes of this type.[1−10] Replacing one pq ligand in $Ru(pq)_3^{2+}$ with phosphines causes the MLCT band to shift to higher energies and decreases the molar absorptivity. This shift can be related to the greater π acceptor ability of a phosphine ligand compared to pq. By facilitating π back-bonding, a phosphine ligand increases the effective positive charge on the Ru center, making it more difficult to ionize, and increasing the energy of the MLCT absorption band. As shown by Kober et al.,[46] the phosphine ligands are increasingly effective as π-acceptors in the order PMe_2Ph < dppm < dppene. This is the same order in which the MLCT bands in the corresponding $[Ru(pq)_2(PP)]^{2+}$ complexes are shifted to higher energies, 442, 417, and 408 nm, respectively. It is also noted that the MLCT bands in the pq−phosphine complexes are red shifted relative to the MLCT bands in the corresponding bpy−phosphine complexes,[34] mostly because of the stabilization of the ligand π^* levels which occurs as the degree of unsaturation increases,[47] but also in part because of the decrease in the ligand field strength as a result of the increased metal−ligand bond distance caused by steric hindrance in the benzo-substituted complex.[13]

Luminescence Properties. The luminescence properties of the complexes in ethanol−methanol rigid glasses at 77 K are given in Table 2. The same luminescence properties are produced whether excitation occurs in the ligand $\pi \rightarrow \pi^*$ states or in the MLCT absorption band, indicating that excitation leads to rapid intramolecular energy transfer to the ^{3}MLCT manifold, which most likely consists of three or four closely spaced levels.[48,49] Luminescence is typically only

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Table 2. Emission Data for $Ru^{II}(pq)_2(PP)^{2+}$ and $Ru^{II}(pq)_3^{2+}$ Complexes[a]

	$\lambda_{em\,max}$ (nm)	ϕ_{em}	τ_{em} (μs)[b]	$k_r \times 10^{-4}$ (s^{-1})[c]	$k_{nr} \times 10^{-4}$ (s^{-1})[d]
$[Ru(pq)_2(Ph_2PCH_2PPh_2)](PF_6)_2$	628 ± 4	0.22 ± 0.02	13	1.7	6.0
$[Ru(pq)_2(Ph_2P(CH_2)_2PPh_2)](PF_6)_2$	588 ± 2	0.22 ± 0.03	15	1.5	5.2
$[Ru(pq)_2(Ph_2P(CH_2)_3PPh_2)](PF_6)_2$	598 ± 2	0.15 ± 0.02	12	1.2	7.1
$[Ru(pq)_2(cis\text{-}Ph_2PCH{=}CHPPh_2)](PF_6)_2$	607 ± 2	0.23 ± 0.03	18	1.3	4.3
$cis\text{-}[Ru(pq)_2(PMe_2Ph)_2](PF_6)_2$	637 ± 5	0.15 ± 0.02	8.6	1.7	9.9
$cis\text{-}[Ru(pq)_2(PMePh_2)_2](PF_6)_2$	619 ± 4	0.12 ± 0.01	11	1.1	8.0
$cis\text{-}[Ru(pq)_2(PPh_3)_2](PF_6)_2$	602 ± 2	0.17 ± 0.02	13	1.3	6.4
$[Ru(pq)_3](ClO_4)_2$	669 ± 2	0.07 ± 0.02	3.8	1.8	24

[a] EtOH−MeOH (4:1); $T = 77$ K. [b] ± 8%. [c] Calculated from ϕ_{em}/τ_{em}. [d] Calculated from $(1 - \phi_{em})/\tau_{em}$.

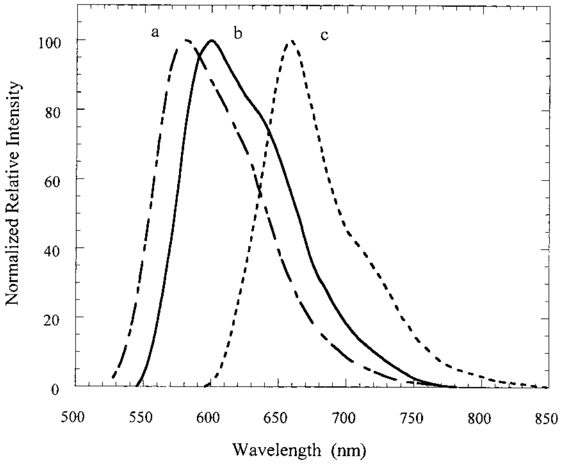

Figure 4. Emission spectra in ethanol−methanol (4:1 v/v) at 77 K of (a) $Ru(pq)_2(dppe)^{2+}$, (b) $Ru(pq)_2(PPh_3)_2{}^{2+}$, and (c) $Ru(pq)_3{}^{2+}$.

observed from the lowest energy ^{3}MLCT state. Figure 4 shows the corrected, normalized emission spectra of $[Ru(pq)_2(Ph_2P(CH_2)_2PPh_2)](PF_6)_2$, $[Ru(pq)_2(PPh_3)_2](PF_6)_2$, and $[Ru(pq)_3](PF_6)_2$ at 77 K. The emission spectra do not possess a well-defined vibrational progression, as is typical for the MLCT excited states with bipyridine,[50] but all of the complexes show a pronounced shoulder on the low-energy side or have a broad structureless emission that tails to lower energy. As with the MLCT absorption maxima, the emission maxima in all the $Ru(pq)_2(PP)^{2+}$ complexes are shifted to higher energies compared to the parent $Ru(pq)_3{}^{2+}$ and to lower energies compared to analogous $Ru(bpy)_2(PP)^{2+}$ complexes.

No detectable luminescence was observed from any of the complexes at room temperature. Approximate measurements of luminescence intensity as a function of temperature with $[Ru(pq)_2(dppene)]^{2+}$ indicated that the intensity falls off rapidly with increasing temperature, becoming very weak above 138 K and undetectable above 250 K. Similar results have been observed with mixed phosphine and arsine bpy complexes[35] and can be attributed to a Ru-based dd state above the MLCT state which is reached by thermal activation. Once populated, the dd state then undergoes rapid decay to the ground state. From electron-transfer theory, the energy of activation, E_a(dd), is expected to be strongly dependent on the relative energies of the MLCT and dd states.[35] A better determination of the position of the dd state relative to the MLCT state will have to await more precise measurements of the temperature dependence of the luminescence.

Table 3. Emission Spectral Fitting Parameters for $Ru^{II}(pq)_2(PP)^{2+}$ and $Ru^{II}(pq)_3{}^{2+}$ Complexes[a]

	E_0 (cm^{-1})	$\hbar\omega_M$ (cm^{-1})	S_M	$\Delta\nu_{1/2}$ (cm^{-1})
$[Ru(pq)_2(Ph_2PCH_2PPh_2)](PF_6)_2$	16 720	1105	1.26	1580
$[Ru(pq)_2(Ph_2P(CH_2)_2PPh_2)](PF_6)_2$	17 270	1260	1.03	1475
$[Ru(pq)_2(Ph_2P(CH_2)_3PPh_2)](PF_6)_2$	16 920	1250	0.97	1450
$[Ru(pq)_2(cis\text{-}Ph_2PCH{=}CHPPh_2)](PF_6)_2$	17 540	1160	1.51	1465
$cis\text{-}[Ru(pq)_2(PMe_2Ph)_2](PF_6)_2$	16 850	1160	1.62	1550
$cis\text{-}[Ru(pq)_2(PMePh_2)_2](PF_6)_2$	16 530	1240	1.14	1450
$cis\text{-}[Ru(pq)_2(PPh_3)_2](PF_6)_2$	16 750	1300	1.24	1430
$[Ru(pq)_3](ClO_4)_2$	15 970	1310	0.80	1350

[a] EtOH−MeOH (4:1); $T = 77$ K. The error limits are as follows: E_0 ± 40 cm^{-1}, $\hbar\omega_M$ ± 40 cm^{-1}, S_M ± 3%, $\Delta\nu_{1/2}$ ± 5%, as determined by using data collected in three separate measurements for each compound.

Table 2 also includes information on the luminescence quantum yields, luminescence lifetimes, and radiative and nonradiative decay rate constants for the bis-pyridylquinoline complexes as well as for the tris-pyridylquinoline complex. The results indicate that the quantum yields of the mixed ligand complexes are increased by a factor of 1.9−3.5 compared to $Ru(pq)_3{}^{2+}$ and the lifetimes are larger by a factor of 2.5−5. Except for the $[Ru(pq)_2(dppp)]^{2+}$ complex, the quantum yields and emission lifetimes of the complexes with chelating phosphine ligands are larger than those of the monodentate ligands. For the three monodentate phosphine complexes, the lifetime increases as the number of phenyl rings attached to phosphorus increases.

Examination of the radiative and nonradiative decay rate constants, derived from the observed lifetimes and quantum yields, reveals that the increase in ϕ_{em} for the phosphine complexes compared to $Ru(pq)_3{}^{2+}$ is due to a large decrease in k_{nr}. The values of k_r for all of the pq complexes are on the order of $1.1-1.7 \times 10^4$ s^{-1}, which is just a little lower than the values of $3-9 \times 10^4$ s^{-1} observed in numerous previous studies of diimine complexes.[8] The large decrease in k_{nr} resulting from the replacement of one pq in $Ru(pq)_3{}^{2+}$ with phosphine ligands is primarily a result of the increase in the energy gap between the ground and excited state, that is, the larger energy gap, E_0, with a smaller contribution coming from the increase in the Huang−Rhys factor, S_M, as discussed later in terms of the spectral fitting parameters.

Spectral Fitting Parameters. The best fit parameters for each compound are listed in Table 3, and emission spectra of $[Ru(pq)_2(dppe)]^{2+}$ and $[Ru(pq)_2(PMePh_2)_2]^{2+}$ complexes are shown in Figure 5 along with the results of the spectral fitting program. Satisfactory results could be obtained with a single mode Franck−Condon analysis. The values of the vibrational acceptor mode, $\hbar\omega_M$, for pq in these complexes

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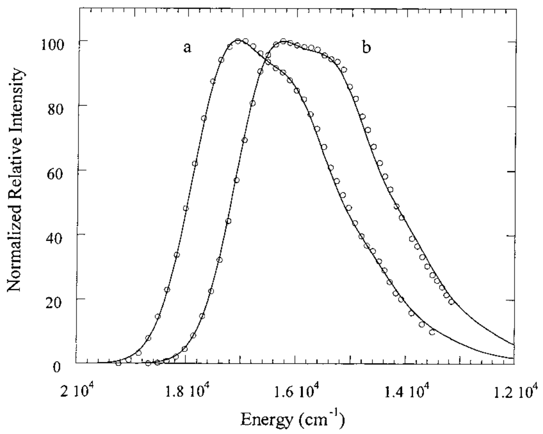

Figure 5. Comparison of experimental emission spectra (○) in ethanol−methanol (4:1 v/v) at 77 K and calculated fits (−) using the spectral parameters in Table 3 for (a) $Ru(pq)_2(dppe)^{2+}$ and (b) $Ru(pq)_2(PMePh_2)^{2+}$.

range from 1105 to 1310 cm^{-1}, which is a little lower than the range of values, 1310−1370 cm^{-1}, used for $[Ru(bpy)_2(L_2)]^{2+}$ complexes,[11,28,44] reflecting the difference between pq and bpy vibrational modes. The Huang−Rhys electron-vibrational coupling constant, S_M, is related to the change in equilibrium displacement between the excited and ground states, ΔQ_e, the reduced mass, M, and the angular frequency, ω, by the equation $S_M = (^1/_2)(M\omega/h)(\Delta Q_e)$. A smaller value of S_M indicates a smaller degree of excited-state distortion relative to the ground state along coordinates coupled to the $^3MLCT \rightarrow {}^1A_1$ relaxation. For the complexes with $Ph_2P(CH_2)_nPPh_2$ ligands, the larger value of S_M when $n = 1$ suggests that the shorter hydrocarbon chain allows a higher degree of distortion at pq in the excited state than is permitted with longer hydrocarbon chains. For the complexes containing monodentate ligands, the values of S_M are generally larger, indicating a greater ability for expansion at pq in the excited state than is possible with the bidentate ligands. The largest value of S_M is obtained for the complex containing the ligands with the fewest phenyl rings, PMe_2Ph, indicating that this ligand allows a greater displacement in the excited state. The S_M value for the $[Ru(pq)_2(Ph_2PCH{=}CHPPh_2)]^{2+}$ complex seems large compared to the value for the $[Ru(pq)_2(Ph_2PCH_2CH_2PPh_2)]^{2+}$ complex, and data for analogous Ru complexes are not available. However, the value[43] of S_M, 1.15, for $[Os(bpy)_2(Ph_2PCH{=}CHPPh_2)]^{2+}$ is 117% larger than the S_M value, 0.53, for $[Os(bpy)_3]^{2+}$, while the value for $[Ru(pq)_2(Ph_2PCH{=}CHPPh_2)]^{2+}$ is 89% larger than the value for $[Ru(pq)_3]^{2+}$.

From radiationless decay theory and the energy gap law,[40,51] the nonradiative decay rate constant, k_{nr}, is known to vary with S_M, E_0, and $\hbar\omega_M$. In simplified form, this relationship can be given as in eq 1[23]

$$k_{nr} \propto e^{-S_M} e^{-\gamma E_0/\hbar\omega_M} \qquad \gamma = (\ln E_0/S_M\hbar\omega_M) - 1 \quad (1)$$

Generally, within experimental error, the data for the complexes follow the energy gap law. For example, the pq complex has the smallest E_0 value, the largest k_{nr} value, and the shortest lifetime, while the dppene complex has the largest E_0 value, the smallest k_{nr} value, and the longest lifetime. The PMe_2Ph complex stands out as a notable exception. Compared to the $PMePh_2$ complex, it has a larger energy gap, E_0, as determined by the spectral fitting, but also a larger k_{nr} value and a shorter lifetime. In this case, the large value of S_M for the PMe_2Ph complex, because of the distortion of pq in its excited state, produces more extensive overlap of the vibrational wave functions for ring-stretching acceptor modes between the ground and excited states. The greater vibrational overlap leads to an enhanced nonradiative decay constant and a shorter excited-state lifetime.

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