128. Spectroscopical and Electrochemical Behavior of New Mixed-Ligand Cyclometalated Rh(III) Complexes

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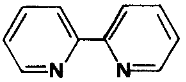
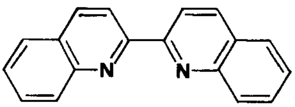
The absorption spectra, luminescence spectra, excited-state lifetimes, and electrochemical behavior of the cyclometalated $[Rh(ppz)_2bpy]^+$, $[Rh(3\text{-}Cl\text{-}ppz)_2(bpy)]^+$, $[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$, $[Rh(ppz)_2(biq)]^+$, and $[Rh(4\text{-}NO_2\text{-}ppz)_2(biq)]^+$ complexes (ppz^-, $3\text{-}Cl\text{-}ppz^-$, and $4\text{-}NO_2\text{-}ppz^-$ are the *ortho*-C-deprotonated forms of 1-phenylpyrazole, 1-(3-chlorophenyl)pyrazole and 1-(4-nitrophenyl)pyrazole, respectively) have been investigated. The results obtained have been compared with those concerning the free protonated ligands and some previously studied mixed-ligand cyclometalated Rh(III) complexes. Luminescence originates from the lowest ligand-centered (LC) excited state, which involves the diimine ligands in all cases except for $[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$, where it involves the *ortho*-metalating ligands. In the absorption spectra, LC and metal-to-ligand charge-transfer (MLCT) bands, involving the diimine and/or the *ortho*-metalating ligands, have been assigned, and correlations between spectroscopic and electrochemical data are discussed.

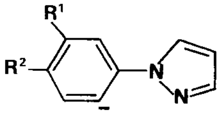
Introduction. – The study of the photochemical, photophysical, and electrochemical behavior of transition-metal complexes is of great interest for both theoretical and practical purposes [1–6]. In the last few years, we have begun a systematic investigation on cyclometalated transition-metal complexes [7–13], a new class of compounds which exhibits interesting excited state properties. Continuing our investigations in this field, we report here results concerning the following new cyclometalated Rh(III) complexes: $[Rh(ppz)_2(bpy)]^+$, $[Rh(3\text{-}Cl\text{-}ppz)_2(bpy)]^+$, $[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$, $[Rh(ppz)_2(biq)]^+$, $[Rh(4\text{-}NO_2\text{-}ppz)_2(biq)]^+$ (ppz^-, $3\text{-}Cl\text{-}ppz^-$, and $4\text{-}NO_2\text{-}ppz^-$) are the *ortho*-C-deprotonated



bpy



biq



ppz^- $R^1 = R^2 = H$
$3\text{-}Cl\text{-}ppz^-$ $R^1 = Cl$, $R^2 = H$
$4\text{-}NO_2\text{-}ppz^-$ $R^1 = H$, $R^2 = NO_2$

forms of 1-phenylpyrazole, 1-(3-chlorophenyl)pyrazole, and 1-(4-nitrophenyl)pyrazole, respectively, bpy is 2,2'-bipyridine, and biq is 2,2'-biquinoline. The results obtained have been compared with those previously reported for similar cyclometalated mixed-ligand Rh(III) complexes.

Experimental. – The preparation, purification, and characterization of $[Rh(ppz)_2(bpy)]^+$, $[Rh(3\text{-}Cl\text{-}ppz)_2(bpy)]^+$, $[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$, $[Rh(ppz)_2(biq)]^+$, $[Rh(4\text{-}NO_2\text{-}ppz)_2(biq)]^+$ as PF_6^- salts have been described in [14]. Butyronitrile was purified according to literature methods. Other solvents and chemicals used were of the best commercial grade. When necessary, the solns. were deaerated by repeated freeze-pump-thaw cycles.

The absorption spectra were recorded with a *Kontron Uvikon 860* spectrophotometer, and the emission spectra (uncorrected) were obtained with a *Perkin Elmer LS 5* spectrofluorimeter equipped with a *Hamamatsu R 928* phototube.

Emission lifetimes were measured with a *Perkin Elmer LS 5* spectrofluorimeter working in phosphorescence mode and with an *Edinburgh 199 DS* single-photon-counting equipment. Single exponential decays were obtained in all cases (estimated error on the lifetime values < 10%).

Emission quantum yields were estimated with the optically diluted method [15], by using $[Ru(bpy)_3]^{2+}$ in aerated aq. soln. as a standard ($\Phi_{em} = 0.028$) [16].

Electrochemical measurements were carried out at r.t. by using a *PAR 273* apparatus. Cyclic voltammograms were obtained in DMF soln.; the working electrodes were a hanging Hg or a Pt electrode. A sat. calomel as reference electrode and a Pt wire as auxiliary electrode were used.

Results and Discussion. – CH_2Cl_2 solutions of the complexes studied were stable in the dark and under laboratory light. Butyronitrile solutions of the complexes containing the biq ligand were unstable even in the dark, giving rise to biq release. The absorption spectra of $[Rh(bpy)(LL)_2]^+$ (LL = ppz^-, $3\text{-}Cl\text{-}ppz^-$, $4\text{-}NO_2\text{-}ppz^-$) and $[Rh(biq)(LL)_2]^+$

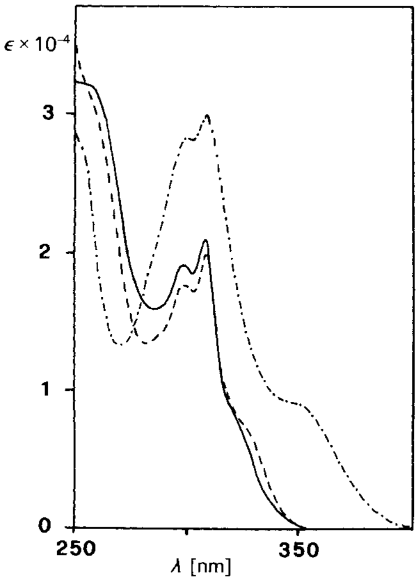


Fig. 1. *Absorption spectra in CH_2Cl_2 solution at room temperature of $[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$ (–·–·–), $[Rh(3\text{-}Cl\text{-}ppz)_2(bpy)]^+$ (– – –) and $[Rh(ppz)_2(bpy)]^+$ (——)*

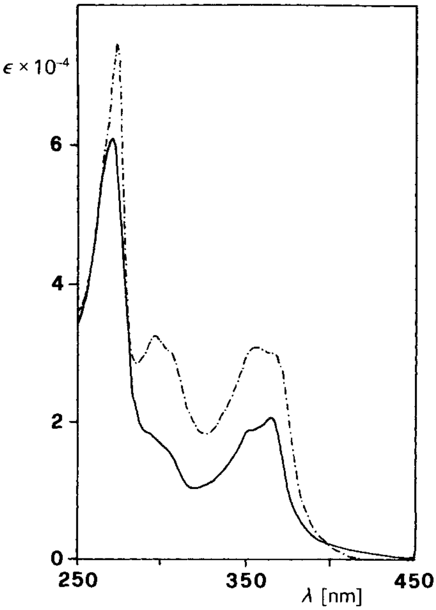


Fig. 2. *Absorption spectra in CH_2Cl_2 solution at room temperature of $[Rh(ppz)_2(biq)]^+$ (——) and $[Rh(4\text{-}NO_2\text{-}ppz)_2(biq)]^+$ (–·–·–)*

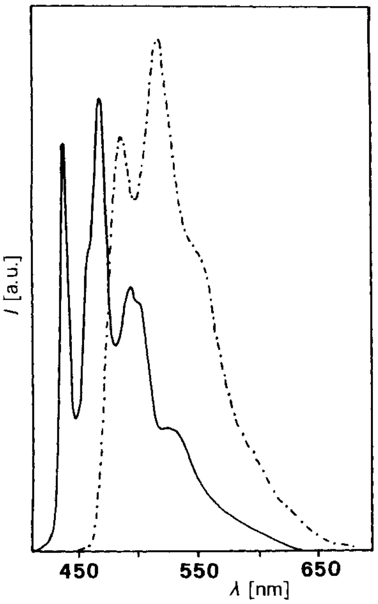


Fig. 3. *Emission spectra in butyronitrile matrix at 77 K of* $[Rh(ppz)_2(bpy)]^+$ (——) *and* $[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$ (–·–·–)

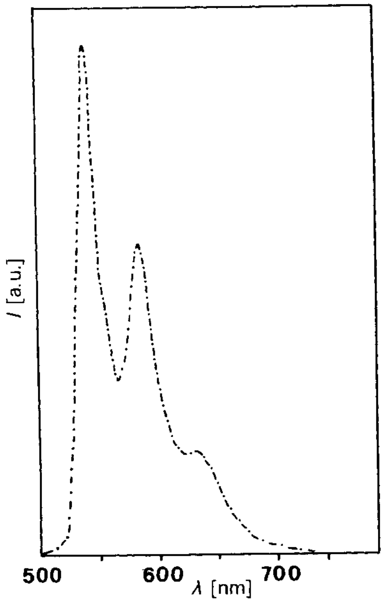


Fig. 4. *Emission spectra in* CH_2Cl_2 *matrix at 77 K of* $[Rh(ppz)_2(biq)]^+$ (–·–·–)

(LL = ppz^-, 4-NO_2-ppz^-) at room temperature, in CH_2Cl_2 solution, are shown in *Figs. 1* and *2* (see also *Table 1*). *Figs. 3* and *4* show the luminescence spectra of the two families of complexes at 77 K, in butyronitrile or in CH_2Cl_2 (for the biq complexes) solution. No evidence for dual emission was obtained for all the complexes examined, and in all cases the luminescence decay was strictly exponential. In fluid solution, the two biq complexes maintain a weak luminescence emission, strongly quenched by oxygen. *Table 1* summarizes the main features of the absorption and emission spectra and shows the emission lifetimes of the five Rh(III) complexes and of their protonated ligands.

In the electrochemical experiments, all the complexes examined showed two or more reversible reduction waves and one irreversible oxidation wave. *Table 2* summarizes the electrochemical behavior of the complexes examined.

The spectroscopic and electrochemical properties of transition-metal complexes are usually discussed in the frame of the 'localized molecular orbital configurations' approach [5] [17]. In such an assumption, the various spectroscopic transitions are classified as metal-centered (MC), ligand-centered (LC), or charge-transfer (CT) (either metal-to-ligand (MLCT) or ligand-to-metal (LMCT)) [5] [17], and the oxidation and reduction processes are classified as metal- or ligand-centered [18]. This simplified approach is not completely satisfactory, if there is a large degree of covalency in the metal–ligand bonds of the ground-state complex, and if excited-state configurations of different nature are sufficiently close in energy to be intermixed. In the cyclometalated complexes, the metal–C^- bonds are indeed expected to exhibit a high degree of covalency, and the LC and MLCT excited configurations may lie very close in energy. For these reasons, the interpretation of the spectroscopic properties of cyclometalated complexes is not easy,

Table 1. *Absorption and Emission Properties of Rh(III) Cyclometalated Complexes and Related Compounds*[a]

	Absorption		Emission			
	293 K		77 K		293 K	
	λ_{max} [nm]	(ε)	λ_{max}[b] [nm]	τ [µs]	λ_{max}[b] [nm]	τ [µs]
$[Rh(ppz)_2(bpy)]^+$	297 307 320	(18000) (20700) (8500)[d]	437[c]	320[c]	–	–
$[Rh(3\text{-}Cl\text{-}ppz)_2(bpy)]^+$	297 307 326	(17800) (20700) (8100)[d]	437[c]	430[c]	–	–
$[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$	297 307 350	(34000) (30000) (12000)[d]	482[c]	1800[c]	–	–
$[Rh(ppz)_2(biq)]^+$	270 355 366	(60000) (19500)[d] (21500)	538	100	547	–
$[Rh(4\text{-}NO_2\text{-}ppz)_2(biq)]^+$	272 296 354	(74000) (32000) (30500)	540	150	548	28[e]
$bpyH^+$[f]	244 281	(7100) (10000)	436	1×10^6	–	–
$biqH^+$[f]	265 289 299 356	(38500) (7500) (6000) (24500)	520	$> 10^5$	–	–
Hppz	255	(15100)	378[c]	$> 10^5$[c]	–	–
3-Cl-ppzH	258	(15500)				–
$4\text{-}NO_2\text{-}ppzH$	228 314	(7500) (38000)			– –	– –

[a] CH_2Cl_2 except where noted. [b] Highest energy feature of the luminescence emission maxima. [c] Butyronitrile glass. [d] Shoulder. [e] Deaerated solution. [f] $MeOH/H_2SO_4$.

Table 2. *Electrochemical Data for Rh(III) Cyclometalated Complexes*

Complex	$E_{1/2}$[a] [V]				
	Oxidation	Reduction			
	I	I	II	III	IV
$[Rh(ppz)_2(bpy)]^+$	+1.27[b]	−1.46	−2.09	–	–
$[Rh(3\text{-}Cl\text{-}ppz)_2(bpy)]^+$	+1.25[b]	−1.42	−2.02	–	–
$[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$	+1.24[b]	−1.16	−1.50	–	–
$[Rh(ppz)_2(biq)]^+$	+1.20[b]	−1.02	−1.64	–	–
$[Rh(4\text{-}NO_2\text{-}ppz)_2(biq)]^+$	+1.08[b]	−0.92	−1.18	−1.33	−1.72

[a] Peak potentials in DMF, 0.1 M TEAP *vs.* SCE at room temperature.

[b] Irreversible wave.

and the localized-molecular-orbital approach can only be used as a first approximation scheme.

Electrochemistry. As shown in *Table 2,* all the complexes examined exhibit at least two reversible (or nearly reversible) reduction waves. This behavior suggests that reduction is a ligand-centered process. $[Rh(ppz)_2(bpy)]^+$ and $[Rh(3\text{-}Cl\text{-}ppz)_2(bpy)]^+$ show two quite similar reduction waves (see *Table 2*), separated by ~ 0.6 V. Since the free 1-phenylpyrazole ligand is much more difficult to reduce than bpy (for Hppz, no reduction wave was observed up to – 2.8 V, whereas the reduction potential of bpy is – 2.2 V [13]), both waves can be assigned to successive one-electron reductions of the bpy ligand. The similarity with the reduction behavior of analogous Rh(III) complexes [8] [10] strongly supports this assignment.

When bpy is replaced with the easier-to-reduce biq ligand, both the waves involving the diimine ligand undergo a strong anodic shift (see *Table 2*). A comparison with similar cyclometalated Rh(III) complexes [10] confirms that for $[Rh(ppz)_2(biq)]^+$ both the reduction waves observed (separated by 0.62 V) are associated with further reductions of the polypyridine ligand.

$[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$ shows two almost reversible reduction waves, at – 1.16 and – 1.5 V. The first one is a non-symmetric wave and appears to result from two overlapping waves separated from each other by less than 0.1 V. Since $4\text{-}NO_2\text{-}Hppz$ is much easier to reduce than bpy ($E_{red}(4\text{-}NO_2\text{-}Hppz) = -1.12$ V, $E_{red}(bpy) = -2.2$ V), the bielectronic wave at – 1.16 V can be related to the one-electron reduction of the two cyclometalated ligands. The second wave, showing the same intensity of the first one, again corresponds to a bielectronic process, and, therefore, can be associated to a further reduction of both the cyclometalated ligands.

$[Rh(4\text{-}NO_2\text{-}ppz)_2(biq)]^+$ shows three reversible reduction waves at – 0.92, – 1.18, and – 1.33 V, and a fourth one, almost reversible, at – 1.72 V. The first one corresponds to the wave observed at – 1.02 V for $[Rh(ppz)_2(biq)]^+$ and can be related to a one-electron reduction of the biq ligand. Its slight shift (0.1 V) towards less negative potentials shows that $4\text{-}NO_2\text{-}ppz^-$ is a weaker electron donor than ppz^-, due to the electron-withdrawing character of the NO_2 substituent. The second and the third waves, separated from each other by ~ 0.15 V, correspond to those, not well resolved, observed for $[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$ at around – 1.1 V and, as in that case, can be assigned to the one-electron reduction of the two cyclometalated ligands. The greater separation between the two waves, compared with the case of $[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$, can be attributed to the presence of the previously reduced biq ligand. In fact, in this complex the ability of the reduced biq ligand to delocalize a further negative charge is lower, compared with that of the non-reduced bpy ligand in the parent bpy complex. Thus, when the first 1-(4-nitrophenyl)pyrazole ligand is reduced, a greater part of the electron density is delocalized on the second cyclometalated ligand in the biq complex compared with the bpy one, and this causes the shift of its reduction potential towards more negative values. The fourth reduction wave, due to its polyelectronic character, could be related to further reduction processes on the polypyridine and cyclometalated ligands.

The oxidation waves, due to their irreversible character, can be associated to metal centered processes.

Luminescence. At 77 K, $[Rh(ppz)_2(bpy)]^+$ and $[Rh(3\text{-}Cl\text{-}ppz)_2(bpy)]^+$ show highly structured emission spectra *(Fig. 3)* and relatively long excited-state lifetimes *(Table 1).*

The spectra are quite similar in energy and shape to those previously reported for $[Rh(bpy)_3]^{3+}$, and assigned to ^{3}LC $\pi \to \pi^*$ transition [8] [20] [21]. Such behavior leads us to assign the emission of both complexes to transitions localized on the bpy ligand. The fact that the lifetime of $[Rh(ppz)_2(bpy)]^+$ and $[Rh(3\text{-}Cl\text{-}ppz)_2(bpy)]^+$ is shorter than that of $[Rh(bpy)_3]^{3+}$, in spite of the same assignment, suggests that the ^{3}LC bpy state responsible for the cyclometalated complexes emission has to be somewhat mixed with a CT level. This expectation is reasonable because in the cyclometalated compounds the stronger σ-donor ability of the NC metalating ligands, compared with that of the polypyridine analogues, increases the negative charge on the metal center and, thus, lowers the energy of the MLCT excited states (see below).

At 77 K, $[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$ exhibits a luminescence emission different in shape, displaced in energy of ~ 2000 cm^{-1} towards the red and with a lifetime longer (1.6 ms) compared with those of $[Rh(ppz)_2(bpy)]^+$ and $[Rh(3\text{-}Cl\text{-}ppz)_2(bpy)]^+$. The very long excited-state lifetime points to a ^{3}LC assignment, but the comparison with the analogous bpy complexes rules out a ^{3}LC bpy assignment. Therefore, the luminescence emission has to be assigned to a ^{3}LC excited-state centered on the $4\text{-}NO_2\text{-}ppz^-$ ligand. The cyclovoltammetric data, showing that the LUMO orbital is centered on the 1-(4-nitrophenyl)pyrazole ligand, strongly support this assignment.

$[Rh(ppz)_2(biq)]^+$ and $[Rh(4\text{-}NO_2\text{-}ppz)_2(biq)]^+$ show very similar, highly structured emission spectra, with maxima at 538 and 540 nm *(Fig. 4)* and lifetimes of 100 and 150 µs, respectively. The spectra are identical in shape and energy, and the excited-state lifetimes are similar to those previously reported for $[Rh(phpy)_2(biq)]^+$ and $[Rh(thpy)_2(biq)]^+$ [10]. For both these complexes, the emission was assigned to transition localized on the biq ligand. Identical assignment is applicable to $[Rh(ppz)_2(biq)]^+$ and $[Rh(4\text{-}NO_2\text{-}ppz)_2(biq)]^+$. Furthermore, it can be noted that, whereas $[Rh(phpy)_2(biq)]^+$ and $[Rh(thpy)_2(biq)]^+$ do not show any luminescence emission at room temperature, the analogous 1-phenylpyrazole compounds show a weak emission band at 548 nm. This behavior suggests that, due to the stronger donor ability of ppz^-, compared with $phpy^-$ and $thpy^-$, for the 1-phenylpyrazole complexes the ^{3}MC excited state moves at higher energy than for $[Rh(phpy)_2(biq)]^+$ and $[Rh(thpy)_2(biq)]^+$, enough to prevent its population (with the consequent fast luminescence decay) at room temperature.

Absorption Spectra. The complexes examined exhibit several intense absorption bands in the near UV spectral region. For the bpy complexes, by analogy with the $[Rh(bpy)_3]^{3+}$ spectrum [20] [21], the high intensity absorption bands with maxima at 297 and 307 nm can be assigned to perturbed LC transitions involving the bpy ligand. For the biq complexes, as previously discussed for similar cyclometalated compounds [10], the high intensity band with λ_{max} at 270 nm can be assigned to transitions localized on the biq ligand. However, in this spectral region contributions of LC transitions involving the cyclometalated ligands have also to be taken into account.

For both families of complexes, the assignment of the absorption bands or shoulders above 310 nm is less straightforward. $[Rh(ppz)_2(bpy)]^+$ and $[Rh(3\text{-}Cl\text{-}ppz)_2(bpy)]^+$ exhibit a not well resolved shoulder at ~ 320 nm and $[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$ a more resolved one at ~ 350 nm, which, from comparison with the absorption spectra of the free ligands *(Table 1)*, cannot be attributed to LC transitions. Neither they can be assigned to MC transitions, due to their high intensity, and also because, for the cyclometalated complexes, being the ligand field strength even higher than for $[Rh(bpy)_3]^{3+}$ (where the lowest

MC bands are expected to lie below 300 nm [8]), such transitions are expected to lie at much higher energy. It follows that the only possible assignments for these shoulders are Rh→bpy and Rh→ppz$^-$ CT transitions. For $[Rh(ppz)_2(bpy)]^+$ and $[Rh(3\text{-}Cl\text{-}ppz)_2(bpy)]^+$, the assignment of the shoulders to Rh→bpy CT transitions can be confidently made considering that: *i*) the cyclovoltammetric data show that the LUMO orbital is centered on the bpy ligand; *ii*) the absorption spectrum of $[Rh(ppz)_2(biq)]^+$ at 320 nm exhibits a minimum. With such an assignment, the absorption shoulder at 320 nm for $[Rh(ppz)_2(bpy)]^+$ and $[Rh(3\text{-}Cl\text{-}ppz)_2(bpy)]^+$ corresponds to the excitation to the lowest singlet-MLCT state, and, assuming that the splitting between the energy of the absorption and emission maxima for MLCT excited states is of the order of $\sim 6000\ cm^{-1}$ (as it seems to be for cyclometalated complexes [13]), the corresponding ^{3}MLCT excited state would be expected to lie at ~ 400 nm, not too far from the ^{3}LC bpy state, responsible for the luminescence emission. This proximity could justify the shorter emission lifetime of $[Rh(ppz)_2(bpy)]^+$ and $[Rh(3\text{-}Cl\text{-}ppz)_2(bpy)]^+$ compared with $[Rh(bpy)_3]^{3+}$ (see above).

For $[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$, the shoulder (observed at ~ 350 nm) cannot be attributed to Rh→bpy CT transition. A comparison of the reduction potentials for $[Rh(ppz)_2(bpy)]^+$ and $[Rh(4\text{-}NO_2\text{-}ppz)_2(bpy)]^+$ shows that the energy of the LUMO orbital centered on the $4\text{-}NO_2\text{-}ppz^-$ is ~ 0.3 eV (~ 2400 cm^{-1}), lower than that of the LUMO orbital centered on the bpy. Therefore, if the Rh→bpy CT transition occurs at ~ 320 nm (31250 cm^{-1}), the Rh→$4\text{-}NO_2\text{-}ppz^-$ is expected to occur at $\lambda \geqslant 347$ nm ($\leqslant 28800\ cm^{-1}$). For this reason, the intense shoulder observed at ~ 350 nm can be attributed to a Rh→$4\text{-}NO_2\text{-}ppz^-$ CT transition.

For $[Rh(ppz)_2(biq)]^+$ and $[Rh(4\text{-}NO_2\text{-}ppz)_2(biq)]^+$, the broad and intense absorption band showed in the spectral region around 360 nm closely corresponds to the lower-energy band of biqH$^+$ [10] and, therefore, can be attributed to LC transition involving the biq ligand. However, some differences in shape and intensity exhibited by the two complexes compared to each other and to the free biq ligand lead us to believe that other types of transitions contribute to this absorption. For the $[Rh(ppz)_2(biq)]^+$, a contribution from a MLCT, Rh→biq transition can be predicted on the basis of a comparison between the reduction potentials of $[Rh(ppz)_2(bpy)]^+$ and $[Rh(ppz)_2(biq)]^+$. It shows that the LUMO biq-centered orbital is 0.44 V (~ 3550 cm^{-1}) lower than the LUMO bpy-centered orbital, therefore, if the Rh→bpy CT transition occurs at ~ 320 nm (~ 31250 cm^{-1}), the Rh→biq CT transition is expected to occur at ~ 361 nm (~ 27700 cm^{-1}), *i.e.* in the above mentioned spectral region. For $[Rh(4\text{-}NO_2\text{-}ppz)_2(biq)]^+$, in addition to the Rh→biq CT transition, a further contribution from a Rh→$4\text{-}NO_2$-ppz CT transition can be predicted. In fact, we have seen before that the MLCT, Rh→$4\text{-}NO_2$-ppz transition has to occur at $\lambda \geqslant 347$ nm, and, thus, it is expected to contribute to the high-energy side of the 360-nm band observed in the absorption spectrum.

In conclusion, for the biq complexes the lower-energy absorption band seems due to the overlapping of one or more CT transitions to the high-intensity LC transition of the biq ligand.

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