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Spectroscopic and Electrochemical Properties of New Mixed-Ligand Orthometalated Rhodium(III) Complexes

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The electrochemical behavior and the absorption spectra, emission spectra, and luminescent lifetimes of the mixed-ligand complexes Rh(phpy)$_2$phen$^+$, Rh(thpy)$_2$phen$^+$, Rh(phpy)$_2$biq$^+$, and Rh(thpy)$_2$biq$^+$ (where phen is 1,10-phenanthroline, biq is 2,2′-biquinoline, and phpy$^-$ and thpy$^-$ are the ortho-C-deprotonated forms of 2-phenylpyridine and 2-(2-thienyl)pyridine) have been studied. The results obtained have been compared with those previously available for the analogous Rh(phpy)$_2$bpy$^+$ and Rh(thpy)$_2$bpy$^+$ complexes (bpy = 2,2′-bipyridine), the [Rh(phpy)$_2$Cl]$_2$ dimer, the homoleptic Rh(phen)$_3$$^{3+}$ species, and the orthometalated Pt(phpy)$_2$(CH$_2$Cl)Cl and Pt(thpy)$_2$(CH$_2$Cl)Cl complexes. The results obtained indicate that, as reported previously by Ohsawa et al., the NN-coordinating ligands are easier to reduce than the NC-orthometalating ligands. The absorption spectra, however, show that the lowest energy MLCT band involves the NC-orthometalating ligands rather than the easier to reduce NN-coordinating ligands. Finally, the luminescence spectra show that the lowest energy excited state is predominantly ligand centered (on the NC-orthometalating ligands when NN = bpy or phen and on the NN-coordinating ligands when NN = biq) in nature. These results show that in these complexes there are several closely spaced levels of different orbital nature and confirm that a localized description of their electronic structure can only be an approximation.

Introduction

In the last few years the attention of numerous research groups has been focused on the search and characterization of polypyridine transition-metal complexes[4-12] that can play the role of light absorption sensitizers (LAS) and/or light emission sensitizers (LES)[13] for the interconversion between light energy and chemical energy via electron-transfer reactions involving electronically excited states.

We have recently begun a systematic investigation on orthometalated transition-metal complexes that constitute a new potential class of mediators for photochemical and chemiluminescent electron-transfer reactions and exhibit other interesting excited state properties. In previous papers we have examined the behavior of orthometalated Pt(II),[14] Pt(IV),[15] and Rh(III)[16] complexes. In this paper we report results concerning the following new orthometalated Rh(III) complexes: Rh(phpy)$_2$phen$^+$, Rh(thpy)$_2$phen$^+$, Rh(phpy)$_2$biq$^+$, and Rh(thpy)$_2$biq$^+$, where phpy$^-$ and thpy$^-$ are the ortho-C-deprotonated forms of 2-phenylpyridine and 2-(2-thienyl)pyridine, phen is 1,10-phenanthroline and biq is 2,2′-biquinoline (Figure 1). The results obtained have been compared with those previously available for the analogous Rh(phpy)$_2$bpy$^+$ [16,17] and Rh(thpy)$_2$bpy$^+$ [16] mixed-ligand complexes, bpy is 2,2′-bipyridine, the [Rh(phpy)$_2$Cl]$_2$ dimer,[18] the homoleptic Rh(phen)$_3$$^{3+}$ species,[19] and the Pt(phpy)$_2$(CH$_2$Cl)Cl and Pt(thpy)$_2$(CH$_2$Cl)Cl complexes.[15]

Experimental Section

The preparation, purification, and characterization of Rh(phpy)$_2$phen$^+$, Rh(thpy)$_2$phen$^+$, Rh(phpy)$_2$biq$^+$, and Rh(thpy)$_2$biq$^+$ as ClO$_4$$^-$ or PF$_6$$^-$ salts have been described elsewhere.[20] Propionitrile and butyronitrile were purified according to literature methods and used in a 4:5 v/v mixture; in the following sections, this mixture will simply be called "nitrile". The other solvents and chemicals used were of the best commercial grade. When necessary, the solutions were deaerated by repeated freeze–pump–thaw cycles.

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

Emission lifetimes were measured with the Perkin-Elmer LS 5 spectrofluorimeter working in phosphorescence mode. Single exponential decays were obtained in all cases (estimated error on the lifetime value <10%). Emission quantum yields were estimated with the optically diluted method[21] by using Ru(bpy)$_3$$^{2+}$ in aerated aqueous solution as a standard (Φ_{em} = 0.028).[22]

Electrochemical measurements were carried out at room temperature by using a Metrohm E/506 Polarecord, a Metrohm E/612 VA scanner, and a Hewlett-Packard 7044 x-y recorder. Cyclic voltammograms were obtained in dimethylformamide (DMF) solution by using a stationary platinum disk or a dropping mercury working electrode, a platinum counter electrode, and an Ag/0.01 AgNO$_3$ reference electrode with TBAP as supporting electrolyte. The electrochemical window examined was between 0.0 and –2.6 V. Scanning speed was 100 mV s^{-1}. The redox potentials of Ru(bpy)$_3$$^{2+}$ under the same experimental conditions were used as a secondary reference for the redox potentials of the new complexes.

Results

Solutions of the four complexes in CH$_2$Cl$_2$ or DMF were stable in the dark and under laboratory light. Nitrile or methanol solutions of the complexes containing the biq ligand were unstable even in the dark, giving rise to ligand release.

The absorption spectra at room temperature and the emission spectra at 77 K of Rh(phpy)$_2$phen$^+$, Rh(thpy)$_2$phen$^+$, Rh(phpy)$_2$biq$^+$, and Rh(thpy)$_2$biq$^+$ are shown in Figures 2 and 3. Less intense ($\epsilon \simeq$ 10–500) shoulders are present in the absorption spectra in the 450–500-nm region. For comparison purposes, the absorption and emission spectra of Rh(phen)$_3$$^{3+}$, Pt(phpy)$_2$(CH$_2$Cl)Cl, and biqH$^+$ are also shown in the same figures. No evidence for dual luminescence emission was obtained, and the luminescence decay was strictly exponential in all cases. In fluid solution, only Rh(thpy)$_2$phen$^+$ maintains a weak luminescence

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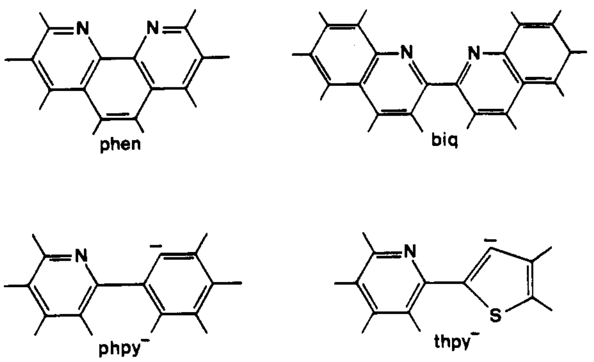

Figure 1. Structural formulas of the ligands.

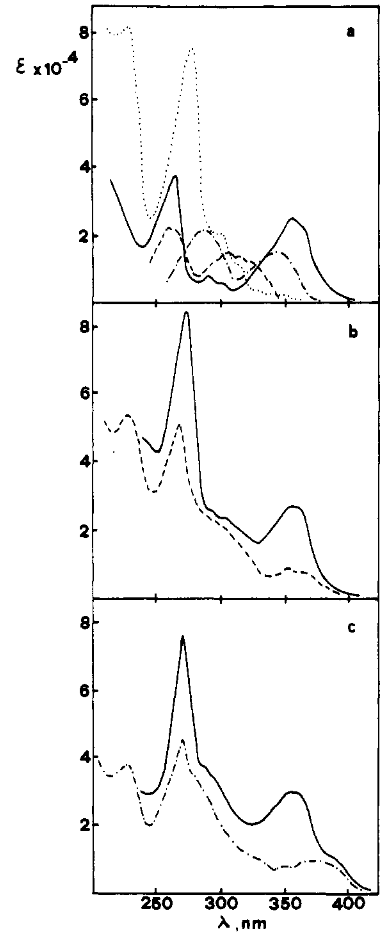

Figure 2. Absorption spectra at room temperature: (a) $Rh(phen)_3^{3+}$ (⋯), $biqH^+$ (—), $Pt(phpy)_2(CH_2Cl)Cl$ (- - -), $Pt(thpy)_2(CH_2Cl)Cl$ (-·-); (b) $Rh(phpy)_2phen^+$ (- - -), $Rh(phpy)_2biq^+$ (—); (c) $Rh(thpy)_2phen^+$ (-·-), $Rh(thpy)_2biq^+$ (—). For the solvent, see table I.

emission ($\Phi \leq 10^{-4}$) in MeOH, strongly quenched by oxygen. Table I summarizes the main features of the absorption and emission spectra and shows the lifetimes of the emitting excited states of the complexes and of some reference compounds.

In the electrochemical experiments (DMF solution, room temperature), three reversible reduction waves were observed. The half-wave reduction potentials for $Rh(phpy)_2phen^+$ and $Rh(phpy)_2biq^+$ are shown in Table II, where the values previously reported for $Rh(phpy)_2bpy^+$ at room temperature[16] and at −54 °C[17] are also listed for comparison purposes. The thpy complexes behave quite similarly to the analogous phpy complexes. In particular, the first and second reduction waves for $Rh(thpy)_2biq^+$ were at −1.02 and −1.63 V vs SCE.

Table I. Absorption and Emission Data for Mixed-Ligand Orthometalated Rh Complexes and Model Compounds

	absorption[a]		emission[b]		
	γ_{max}, nm	$10^{-3}\epsilon$	γ_{max},[c] nm	τ, ms	ref
$Rh(phpy)_2bpy^+$	239	53	454	0.17	16, 17
	257	55			
	296	36			
	367	8			
$Rh(phpy)_2phen^+$	227	53.7	454	0.19	*d*
	265	50.8			
	355	6.9			
	(370 sh)	5.9			
$Rh(phpy)_2biq^+$ [e]	270	86	544	0.08	*d*
	360	27.5			
$Rh(thpy)_2bpy^+$	263	26	521[f]	0.50	16
	295	31			
	379	9			
$Rh(thpy)_2phen^+$	227	36	521[f]	0.50	*d*
	272	44.5			
	353	7.2			
	380	8.5			
$Rh(thpy)_2biq^+$ [e]	272	77.5	546	0.04	*d*
	363	29.4			
	(380 sh)	15			
	Model Compounds				
$Rh(phen)_3^{3+}$	222	78	450[g]	48	19
	279	75.5			
	304	20			
	314	10.4			
	334	4.2			
	350	3			
$Pt(phpy)_2(CH_2Cl)Cl$	260[e]	23	444	0.30	15
	306	15			
$Pt(thpy)_2(CH_2Cl)Cl$	287[e]	22	507	0.34	15
	344	17			
$biqH^+$ [h]	265	38.8	520	>100	*d*
	289	7.5			
	299	6.0			
	356	24.5			

[a] MeOH solution, at room temperature, unless otherwise noted. [b] Nitrile solution at 77 K, unless otherwise noted. [c] λ of the highest energy feature of the phosphorescence emission. [d] This work. [e] CH_2Cl_2 solution. [f] In deaerated MeOH solution at room temperature λ_{max} = 526 nm and τ = 1.0 μs. [g] MeOH/EtOH (1:5 v/v). [h] $MeOH/H_2SO_4$.

Table II. Reduction Potentials[a]

	$E_{1/2}$,[b] V			
	+/0	0/−	−/2−	ref
$Rh(phpy)_2bpy^+$ [c]	−1.84	−2.49	−2.76	17
$Rh(phpy)_2bpy^+$	−1.41			16
$Rh(phpy)_2phen^+$	−1.43	−2.12	−2.42	*d*
$Rh(phpy)_2biq^+$	−1.00	−1.60	−2.40	*d*

[a] Room temperature, DMF solutions, 0.1 M TBAP, unless otherwise noted. [b] Half-wave reduction potentials vs SCE, unless otherwise noted. [c] −54 °C, DMF, 0.1 M TEAH, vs $Fc^{+/0}$. [d] This work.

Discussion

Absorption Spectra. The complexes examined exhibit several intense absorption bands in the near-UV spectral region. Because of the high degree of covalency of the C^-–Rh bonds, a localized description of the electronic structure of these complexes may not be completely satisfactory, but it will be used for sake of simplicity. As discussed elsewhere for $Rh(phpy)_2(bpy)^+$ and for analogous complexes,[16-18] the bands that appear in the observed spectral region can only be due to ligand-centered (LC) or metal-to-ligand charge-transfer (MLCT) transitions. To facilitate the assignment, comparison with spectra of compounds containing the same ligands but not showing MLCT bands is most useful. As model compounds for the LC bands of coordinated phen, phpy, and thpy, we have chosen $Rh(phen)_3^{3+}$,[19] $Pt(phpy)_2(CH_2Cl)Cl$,[15] and $Pt(thpy)_2(CH_2Cl)Cl$.[15] For coordinated biq, lacking any well-defined complex not showing MLCT bands, the protonated species $biqH^+$ has been considered. This last choice is justified by the close similarity between the spectra of $Rh(phen)_3^{3+}$ and $phenH^+$.[19]

As one can see from Figure 2, the band with λ_{max} = 227 nm that is present in the spectra of $Rh(phpy)_2phen^+$ and $Rh(thpy)_2phen^+$ corresponds quite well to the band with λ_{max} = 222

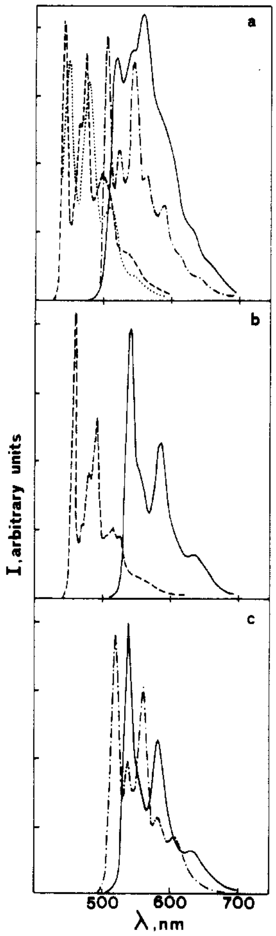

Figure 3. Emission spectra at 77 K: (a) $Rh(phen)_3^{3+}$ (···), $biqH^+$ (—), $Pt(phpy)_2(CH_2Cl)Cl$ (- - -), $Pt(thpy)_2(CH_2Cl)Cl$ (-·-); (b) $Rh(phpy)_2phen^+$ (- - -), $Rh(phpy)_2biq^+$ (—); (c) $Rh(thpy)_2phen^+$ (-·-), $Rh(thpy)_2biq^+$ (—). For the solvent, see table I.

nm of $Rh(phen)_3^{3+}$ and can thus be assigned to transitions localized on the phen ligand. In the same way, the bands with maximum at 265 nm for $Rh(phpy)_2(phen)^+$ and at 272 nm for $Rh(thpy)_2(phen)^+$ closely correspond to the LC band of $Rh(phen)_3^{3+}$ with λ_{max} = 279 nm. One reason for the slightly different λ_{max} values is presumably the contribution of lower intensity LC transitions of the phpy and thpy ligands, whose maxima lie at 260 and 287 nm, respectively, in their Pt(IV) complexes (Figure 2, Table I). The bands with λ_{max} at 270 and 272 nm of $Rh(phpy)_2biq^+$ and $Rh(thpy)_2biq^+$ are quite similar to the band of $biqH^+$ with λ_{max} = 265 nm and can thus be assigned to transitions localized on the biq ligand. This seems also to be the case for the broad band of $Rh(phpy)_2biq^+$ and $Rh(thpy)_2biq^+$ with λ_{max} at ~360 nm, which closely corresponds in energy and intensity to the $biqH^+$ band with λ_{max} = 356 nm. At least part of the composite absorption that appears with more or less intensity for all the complexes studied around 300 nm can also be assigned to LC transitions because all of the ligands show absorption bands in that region.

Above 340 nm, $Rh(phpy)_2phen^+$ and $Rh(thpy)_2phen^+$ show broad, relatively intense bands with maximum at 355 and 380 nm, respectively, quite similar in energy, shape, and intensity to those shown by $Rh(phpy)_2bpy^+$ and $Rh(thpy)_2bpy^+$. As previously discussed,[16] such bands are not present in the model compounds for the LC bands and thus they must be attributed to MLCT transitions. Specific assignment to MLCT transitions involving either the polypyridine ligand or the orthometalating ligand is not easy. In a previous paper,[16] we have assigned the band at 379 nm of $Rh(thpy)_2bpy^+$ to a Rh → $thpy^-$ transition and, tentatively, the 367-nm band of $Rh(phpy)_2bpy^+$ to a Rh → $phpy^-$ transition. Ohsawa et al.,[17] however, have assigned the latter band to a Rh → bpy transition. Examination of the spectra of $Rh(phpy)_2biq^+$ and $Rh(thpy)_2biq^+$ helps to resolve the above controversy. Biq is much easier to reduce than bpy, and in the Ru(II) complexes the Ru → biq CT bands are red shifted by ~3000 cm^{-1} compared to the Ru → bpy CT ones.[12,23] Thus, if the bands at 367 and 380 nm of $Rh(phpy)_2bpy^+$ and $Rh(thpy)_2bpy^+$ were due to Rh → bpy CT transitions, adsorption bands due to Rh → biq CT transitions would be expected at about 410 and 430 nm, respectively, for the two Rh complexes containing the biq ligand. No band of reasonable intensity, however, is present in this spectral region. Conversely, a CT absorption is clearly present for $Rh(thpy)_2phen^+$ and $Rh(thpy)_2biq^+$ at 380 nm, i.e. at practically the same wavelength of the CT band previously observed for $Rh(thpy)_2bpy^+$. This strongly suggests that this band is due to a Rh → $thpy^-$ transition, substantially unaffected by the nature of the polypyridine ligand. Preliminary results on the thermal reaction of $Rh(thpy)_2biq^+$ in AN solution show that the substitution of the biquinoline ligand by the solvent causes the disappearance of the lowest energy LC band centered at 363 nm (which is only present in coordinated biq and in $biqH^+$) and clearly reveals the presence of a band centered at 380 nm. This band does not change its position and intensity during the substitution reaction and is quite similar in shape and energy to that observed for $Rh(thpy)_2bpy^+$ and $Rh(thpy)_2phen^+$, again supporting a Rh → $thpy^-$ assignment for the 380-nm absorption of the thpy complexes. By analogy, the bands around 360 nm for $Rh(phpy)_2bpy^+$ and $Rh(phpy)_2phen^+$ can be due to Rh → $phpy^-$ CT transitions. The presence of a similar band in the $[Rh(phpy)_2Cl]_2$ dimer[18] reinforces this assignment. In $Rh(phpy)_2biq^+$, this band is apparently hidden under the broad, intense ligand-centered biq band with λ_{max} = 360 nm.

Finally, the shoulders at long wavelength (~450–500 nm) could correspond to metal-enhanced singlet → triplet absorption of the ligands, as previously proposed for $Cr(bpy)_3^{3+}$.[24]

Emission Spectra. At 77 K, $Rh(phpy)_2phen^+$ and $Rh(thpy)_2phen^+$ show highly structured emission spectra (Figure 3) and relatively long excited-state lifetimes (Table I). The spectra are identical in energy and shape with those previously reported for $Rh(phpy)_2bpy^+$ [16,17] and $Rh(thpy)_2bpy^+$,[16] respectively, and the excited-state lifetimes have almost the same values as those of the analogous bpy complexes. Furthermore $Rh(thpy)_2phen^+$ shows a weak emission band at room temperature with lifetime (1 μs) and quantum yield ($\leq 10^{-4}$) that are the same as those observed for $Rh(thpy)_2bpy^+$. For both $Rh(phpy)_2bpy^+$ [16,17] and $Rh(thpy)_2bpy^+$,[16] the emission was assigned to transitions localized on the $phpy^-$ and $thpy^-$ ligands, with some mixing between the lowest ^3LC $phpy^-$ state and a ^3MLCT level in the case of the former complex.[16] The identical experimental behavior of the phen complexes compared to that of the bpy ones leads us to an identical assignment.

$Rh(phpy)_2biq^+$ and $Rh(thpy)_2biq^+$ show very similar highly structured emission spectra with maxima at 544 and 546 nm (Figure 3) and lifetimes of 80 and 40 μs, respectively. The structured emissions and the relatively long lifetimes rule out a triplet metal-centered (MC) emission. The different shapes of the emission spectra compared to that of the "bona fide" ^3LC $phpy^-$ and $thpy^-$ emitters ($Pt(phpy)_2(CH_2Cl)Cl$ and $Pt(thpy)_2(CH_2Cl)Cl$, respectively) and the shorter lifetimes in spite of the fact that Rh is lighter than Pt are not consistent with emission from a ^3LC excited state localized on the orthometalating ligands. The similarity of the emission spectra of the two biq compounds is also not consistent with a MLCT transition involving different orthometalating ligands and suggests that the only possible assignments for these bands are either a LC transition centered on the biq ligand or a Rh → biq CT transition. The assignment of the luminescence emission to a ^3LC excited state centered on the biq ligand is reasonable in view of the following considerations:

(i) The emission spectra are very close in energy (850 cm^{-1}) to that of the protonated free biq ligand. (Table I)

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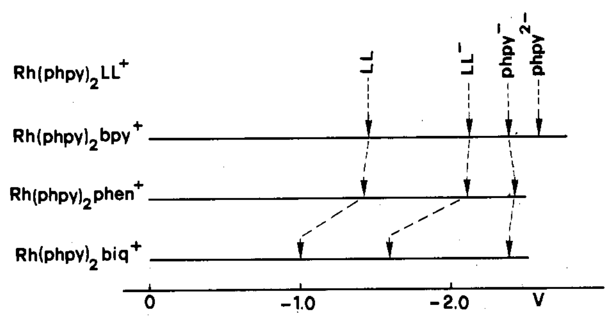

Figure 4. Correlation among the reduction potentials (vs SCE) of Rh$(phpy)_2LL^+$ complexes. The reduction potentials of $Rh(phpy)_2bpy^+$, reported by Ohsawa et al. vs $fc^{+/0}$,[17] have been displaced by +0.365 V.

(ii) The emission lifetimes at 77 K (80 μs) are longer than those expected for ^{3}MLCT excited states (1–10 μs)[12,14,16–18,25] and are comparable to the lifetime of the luminescence of $[Rh(phpy)_2Cl]_2$ (93 μs), assigned to LC emission.[18]

(iii) If the assignment of the lowest absorption band to a LC biq transition is valid (vide supra), the lowest excited state cannot be a CT level because the singlet–triplet splitting is expected to be larger for LC than for CT excited states. Assuming that the splitting between the energy of the absorption and emission maxima for MLCT excited states is on the order of 5000 cm^{-1} as for $Ru(bpy)_3^{2+}$ [12] and Pt(II) orthometalated complexes[14] and taking the absorption at 380 nm for $Rh(thpy)_2biq^+$ as a singlet MLCT band (see above), the corresponding ^{3}MLCT emission would be expected to occur at 475 nm, whereas the emission is actually observed at 544 nm.

Electrochemistry. The electrochemical behavior of Rh$(phpy)_2bpy^+$ has been carefully investigated by Ohsawa, et al.,[17] in DMF at −54 °C. Under such conditions, four reversible reduction waves were observed (Table II). On the basis of the similarity with the reduction pattern observed for the analogous IR complex and the known behavior of the homoleptic Ru$(bpy)_3^{2+}$,[8,26] $Ir(bpy)_3^{3+}$,[27] and $Ir(phpy)_3$[17] complexes, it was suggested that the various reduction waves correspond to processes associated not only with ligand-localized acceptor orbitals but also with acceptor orbitals that are localized on specific ligands. Thus, the first reduction wave was assigned to reduction of the bpy ligand, and the group of three closely spaced waves was associated with reduction at the previously reduced bpy and the two $phpy^-$ ligands. The results obtained for $Rh(phpy)_2phen^+$ and Rh$(phpy)_2biq^+$, which refer to room temperature solutions and are limited to a narrower potential window, fit nicely with those of Ohsawa, et al.[17] (Figure 4). As one can see, when bpy or phen is replaced with the easier to reduce biq ligand, the first and the second wave undergo a strong anodic shift, whereas the third reduction wave is almost unaffected. This confirms that the first reduction wave is associated with reduction of the polypyridine ligand and also demonstrates that the second reduction wave is associated with further reduction of the same ligand. Reduction of the orthometalating ligands takes place only at more negative potentials.

Conclusions. For the widely studied family of Ru(II)–polypyridine complexes, it has generally been found that there is a correlation between spectroscopic and electrochemical properties.[12,26,28–32] The reasons for such a correlation lies in the fact that the LUMO/π^* ligand orbital is involved both in the first electrochemical reduction process and in the light-induced "internal" redox process (i.e., in the MLCT excitation) that gives rise to the lowest energy spin-allowed and spin-forbidden transitions (i.e., to the lowest energy intense absorption band and to the luminescene band).

The results obtained with the mixed-ligand $Rh(phpy)_2LL^+$ and $Rh(thpy)_2LL^+$ family (LL = bpy[16,17], phen, biq) indicate that these complexes behave quite differently from the Ru(II)–polypyridine complexes. The cyclic voltammetric data (Figure 4) clearly indicate that the NN-coordinating ligands are easier to reduce than the NC-metalating ligands, as was also previously observed by Ohsawa et al.[17] This shows that the LUMO is a π^* orbital essentially localized on the NN-coordinating ligands. The absorption spectra, however, show that the lowest energy MLCT band involves the NC-metalating ligands rather than the easier to reduce NN-coordinating ligands. The reason why the energies of the Rh → NC and Rh → NN MLCT transitions do not reflect the relative energies of the corresponding π^* ligand orbitals (i.e., the failure of Koopman's theorem) is probably 2-fold: (i) the t_{2g} (octahedral) d metal orbitals are split because of the different donor ability of the NN and NC ligands, with the d orbitals involved in the Rh → NC transitions lying at higher energies than that involved in the Rh → NN transition; (ii) because of the different covalent character of the Rh–NC and Rh–NN bonds, the difference between the interelectronic repulsions on one-electron reduction of the NC and NN ligand may be quite different from the difference between the interelectronic repulsions on one-electron excitation to the same ligands. More generally, it should be noted that the simplified picture based on metal or ligand localization of the electrons involved in spectroscopy and electrochemistry (widely used for transition-metal compounds including the Ru (II)–polypyridine complexes) cannot give a fully satisfactory description for systems like the orthometalated complexes where there is a large degree of covalency in the metal–ligand bonds.

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Registry No. $biqH^+$, 59219-37-3; $[Rh(phpy)_2phen]PF_6$, 114533-71-0; $[Rh(phpy)_2biq]PF_6$, 114550-25-3; $[Rh(thpy)_2phen]PF_6$, 114550-23-1; $[Rh(thpy)_2biq]PF_6$, 114533-73-2.

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