16. Spectroscopic and Electrochemical Behavior of Cyclometalated Pd(II) Complexes

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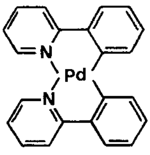
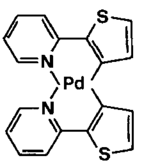
(23.XI.87)

The absorption and emission spectra, emission lifetimes, luminescence quantum yields, and electrochemical behavior of the complexes $\mathrm{Pd(Phpy)_2}$, $\mathrm{Pd(Thpy)_2}$, and $\mathrm{Pd(bhq)_2}$ ($\mathrm{Phpy^-}$, $\mathrm{Thpy^-}$, and $\mathrm{bhq^-}$ are the deprotonated forms of 2-phenylpyridine, 2-(2-thienyl)pyridine, and benzo[*h*]quinoline, respectively) have been studied, and the results obtained have been compared with those available for Pt(II) and Pt(IV) complexes containing the same ligands. The intense ligand-centered absorption bands below 340 nm are strongly perturbed by metalation, and the absorption features in the 340–450-nm region are likely to include contributions from formally metal-to-ligand charge-transfer transitions. The structured luminescence spectra observed at 77 K (lifetimes are 0.48, 0.28, and 2.6 ms for $\mathrm{Pd(Phpy)_2}$, $\mathrm{Pd(Thpy)_2}$, and $\mathrm{Pd(bhq)_2}$, respectively) have been assigned to transitions having mainly ligand-centered character, with an increasing metal-to-ligand charge-transfer contribution in going from $\mathrm{Pd(bhq)_2}$ to $\mathrm{Pd(Phpy)_2}$ and to $\mathrm{Pd(Thpy)_2}$. The complexes $\mathrm{Pd(phpy)_2}$ and $\mathrm{Pd(thpy)_2}$ show two reversible one-electron reduction waves, whereas reduction of $\mathrm{Pd(bhq)_2}$ is irreversible, as is the oxidation of the three complexes.

Introduction. – In the last decade, a great deal of attention has been devoted to electron-transfer reactions involving light, because they are quite interesting for fundamental reasons and very promising for practical applications [1–7]. Transition-metal complexes having appropriate photochemical, photophysical, and redox properties are ideal candidates to play the roles of reactants and/or mediators in the processes [8] [9]. The exhaustive search for suitable compounds whithin the Ru(II) polypyridine family [9] [10] has recently been accompanied by an increasing interest towards cyclometalated complexes containing ligands which are structurally similar to polypyridines [11–22]. Continuing our investigations [17–21] on the photochemical, photophysical, and electrochemical behavior of cyclometalated complexes, we have studied the Pd(II) complexes of the deprotonated forms of 2-phenylpyridine ($\mathrm{Phpy^-}$), 2-(2-thienyl)pyridine ($\mathrm{Thpy^-}$), and benzo[*h*]quinoline ($\mathrm{bhq^-}$). The results obtained are discussed and compared with those previously obtained for the analogous Pt(II) [17] and Pt(IV) [18] complexes.



$\mathrm{Pd(Phpy)_2}$



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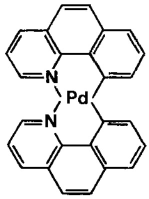

$\mathrm{Pd(Bhq)_2}$

Experimental. – The preparation, purification, and characterization of *cis*-Pd(Phpy)$_2$, *cis*-Pd(Thpy)$_2$, and *cis*-Pd(bhq)$_2$ will be reported elsewhere [20]. Butyronitrile was purified according to literature methods. The other solvents were of the best commercial grade. The absorption spectra were recorded with a *Kontron Uvikon 860* spectrophotometer. The emission spectra and luminescence lifetimes (in butyronitrile solns. at 77 K) were obtained with a *Perkin-Elmer LS5* spectrofluorimeter equipped with an *Hamamatsu R928* phototube. Emission quantum yields at low temp. in MeOH/EtOH 1:5 were estimated by means of an *Oxford* liq. N_2 *DN704* cryostat adapted to a *Perkin-Elmer MPF66* spectrofluorimeter, using $Rh(phen)_3^{3+}$ as a standard [24]. Electrochemical measurements were carried out in DMF soln. with TBAP as supporting electrolyte by an *Amel Electrochemolab* multipurpose system equipped with a *Tektronix RM564* storage oscilloscope. The working electrodes were a dropping Hg electrode and a Pt electrode for cathodic and anodic processes, respectively. A saturated calomel reference electrode and a Pt counter electrode were also used, separated by the test soln. *via* fine fritted glass disks. The potentials reported are *vs.* SCE.

Results. – The complexes examined were thermally stable in all the solvents used during the time periods of the experiments, but a decrease ($\approx$ 10%) of the intensity of the lowest-energy bands was observed in butyronitrile and MeOH after 24 h.

The absorption spectra of the three complexes in butyronitrile solutions at room temperature between 250 and 450 nm are shown in *Fig. 1*. In the same figure, the absorption spectra of the free C-protonated ligands are also reported for comparison purposes.

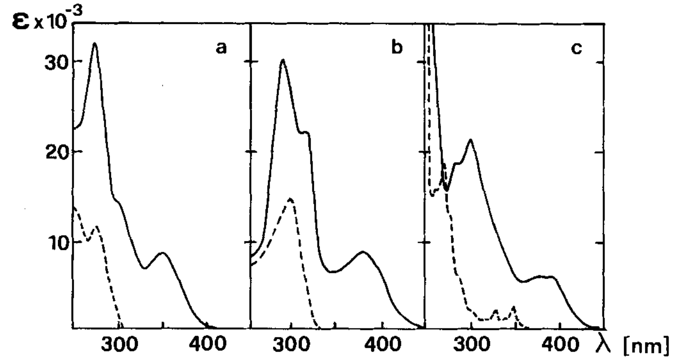

Fig. 1. *Absorption spectra of* a) *Pd(Phpy)$_2$ (—) and HPhpy (---)*; b) *Pd(Thpy)$_2$ (—) and HThpy (---)*; c) *Pd(bhq)$_2$ (—) and Hbhq (---) in butyronitrile at room temperature*

The luminescence spectra of the three complexes in butyronitrile solutions at 77 K are reported in *Fig. 2*, again with the spectra of the free ligands, The emission decay was strictly exponential in all cases, and the values obtained for the lifetimes are reported in *Table 1*. The emission quantum yields in MeOH/EtOH 1:5 at 77 K are also shown in *Table 1*. On increasing temperature, the luminescence intensity became weaker, and no emission could be detected at room temperature.

In the electrochemical experiments (DMF, room temperature), Pd(Phpy)$_2$ and Pd(Thpy)$_2$ showed two reversible one-electron reduction waves, whereas the reduction of Pd(bhq)$_2$ exhibited irreversible character. On oxidation, all the complexes showed an irreversible wave. The potentials are indicated in *Table 1*.

Discussion. – The spectroscopic and electrochemical properties of transition-metal complexes are usually discussed with the assumption that the ground state as well as the excited and the redox states involved can be described in a sufficiently approximate way by localized molecular-orbital configurations [25]. With such an assumption, the various

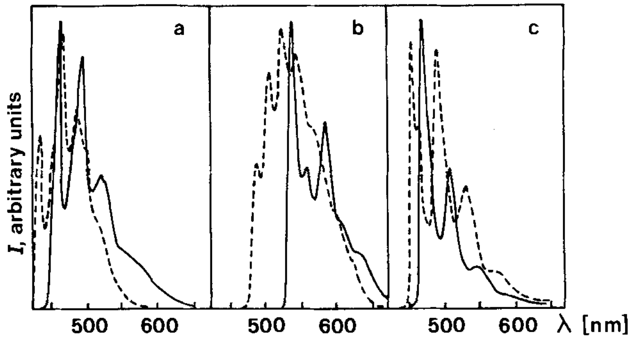

Fig. 2. *Emission spectra of* a) *Pd(Phpy)$_2$* (——) *and HPhpy* (- - -); b) *Pd(Thpy)$_2$* (——) *and HThpy* (– – –); c) *Pd(bhq)$_2$* (——) *and Hbhq* (– – –) *in butyronitrile at 77 K*

Table 1. *Absorption, Emission, and Electrochemical Data for Pd(II) Complexes*

Complex	Absorption[a][b]		Emission[a][c]			E_p[d] [V]		
	λ_{max} [nm]	ε	λ_{max}[e] [nm]	τ[f] [µs]	Φ_{em}	+/0	0/−	−/2−
Pd(Thpy)$_2$	400 (sh) 380 291	7500 8600 29800	536	280	~ 1	+ 1.23[g]	− 1.96	− 2.24
Pd(Phpy)$_2$	349 272	8800 32200	458	480	$< 10^{-2}$	+ 1.38[g]	− 2.04	− 2.29
Pd(bhq)$_2$	391 376 298	5900 5900 21600	472	2600	$< 10^{-2}$	+ 1.27[g]	− 1.85[g]	− 2.05[g]

[a] In butyronitrile. [b] 293 K. [c] 77 K. [d] Peak potentials in DMF, TEAP 0.1 M *vs.* SCE. [e] Wavelength of the highest energy feature of the phosphorescence emission. [f] Estimated error ± 10%. [g] Irreversible wave.

spectroscopic transitions are classified as metal-centered (MC), ligand-centered (LC), or charge-transfer (either metal-to-ligand (MLCT) or ligand-to-metal (LMCT)) [25], and the oxidation and reduction processes are classified as metal- or ligand-centered [26]. This simplified picture, of course, is no longer applicable, 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 [25] [26].

Contrary to what happens for 2,2′-bipyridine and 1,10-phenanthroline, for Phpy$^-$, Thpy$^-$, and bhq$^-$ the two halves of the bidentate ligands are different. Furthermore, the metal–C$^-$ bond is expected to exhibit a higher degree of covalency than the metal–N bond. It follows that in the cyclometalated complexes, the LC transitions may exhibit a considerable (intra-ligand) charge-transfer character, while the charge trasferred in the nominally MLCT transitions may be very small. Mixing of LC and MLCT excited configurations may also occur, because they are close in energy. For all these reasons, the interpretation of the properties of cyclometalated complexes is not easy and can hardly be enclosed in the simplified frame used for the polypyridine complexes [9] [10]. Comparison of the results obtained for different metals or for the same metal in different oxidation states may reveal trends capable of giving guidelines for a correct interpretation.

Absorption Spectra. The complexes examined show intense absorption bands in near-UV spectral region *(Fig. 1)*. The bands with maxima below 340 nm can be assigned to metal-perturbed LC transitions, since the C-protonated forms of the cyclometalated ligands exhibit more of less similar bands in the same spectral region. The less intense bands above 340 nm are difficult to assign. Strongly metal-perturbed LC transitions may contribute to the absorption in this region, but it seems likely that bands of other orbital nature are also present. Contribution from MC transitions is unlikely to be important for absorptions showing extinction coefficients of several thousands. On the other hand, LMCT bands are unlikely to appear at such relatively low energies, because Pd(II) is difficult to reduce. Thus, in the framework of a localized-configuration treatment, the most plausible assignment for these bands remains that of MLCT transitions. The presence of similar bands at somewhat lower energies in the analogous Pt(II) complexes is consistent with such assignment, as is the absence of such bands in the Pt(IV) complexes. An alternative approach to the problem based on a non-localized description of the various states would probably be more correct, but would need a better knowledge of the detailed electronic situation of the molecule.

Emission Spectra. Table 2 summarizes the luminescence properties of the Pd(II) complexes as well as those of the free ligands and of related Pt(II) and Pt(IV) complexes.

For $Pd(bhq)_2$, the assignement of the luminescence emission to an essentially ^{3}LC excited state can confidently be made on the basis of the following considerations: *i)* the emission spectrum is only slightly red-shifted (650 cm^{-1}) with respect to the spectrum of the free C-protonated ligand; *ii)* the relative intensities of the vibrational features are quite similar to those of the ligand; *iii)* the radiative lifetime (estimated from the experimental lifetime and quantum yield) is > 0.25 s, a value expected for slightly metal-perturbed ^{3}LC emissions.

For $Pd(Phpy)_2$, *i)* the red-shift from the spectrum of the C-protonated ligand is larger ($\sim$ 1400 cm^{-1}), *ii)* the relative intensities of the vibrational features are different, and *iii)* the radiative lifetime is estimated to be > 0.05 s. Therefore, the luminescent excited state is mainly ^{3}LC in nature, but some MLCT contribution is present.

For $Pd(Thpy)_2$, *i)* red-shift from the spectrum of the free C-protonated ligand is even larger ($\sim$ 1900 cm^{-1}), *ii)* the relative intensities of the vibrational structure is quite

Table 2. *Emission Data for Pd(II) Complexes and Related Compounds*[a])

Compound	E[b]) [cm^{-1}]	τ [µs]	Ref.
$Pt(Thpy)_2$	17500	12.0	[17]
$Pd(Thpy)_2$	18700	280	This work
$Pt(Thpy)_2(CH_2Cl)Cl$	19700	340	[18]
HThpy	20600	3.5×10^4	[17]
$Pt(Phpy)_2$	20400	4.0	[17]
$Pd(Phpy)_2$	21800	480	This work
$Pt(Phpy)_2(CH_2Cl)Cl$	22500	300	[18]
HPhpy	23300	$> 1 \times 10^5$	[17]
$Pt(bhq)_2$	20300	6.5	[17]
$Pd(bhq)_2$	21200	2600	This work
Hbhq	21800	$> 1 \times 10^5$	[17]

[a]) In butyronitrile or butyronitrile/propionitrile at 77 K.

[b]) Highest-energy feature of the phosphorescence emission.

different, and *iii*) the radiative lifetime is estimated to be ~ 3×10^{-4} s. These results suggest that the luminescence of $Pd(Thpy)_2$ originates from a triplet level which receives contributions from both LC and MLCT configurations. This suggestion is supported by the following consideration: taking the absorption at ~ 400 nm as a singlet MLCT band and assuming that the splitting between absorption and emission maxima for MLCT excited states is ~ 5000 cm^{-1} (as for $Ru(bpy)_3^{2+}$ and for the cyclometalated Pt(II) complexes), the MLCT emission should occur at ~ 500 nm, a wavelength that is not too far from the observed emission (536 nm).

In conclusion, the luminescence emission observed at 77 K for the Pd(II) cyclometalated complexes originates from ^{3}LC levels exhibiting an increasing MLCT contribution in going from $Pd(bhq)_2$ (which exhibits almost pure ^{3}LC emission) to $Pd(Phby)_2$ and $Pd(Thpy)_2$. Comparison with the spectra and lifetimes of the previously studied Pt(II) and Pt(IV) complexes *(Table 2)* containing the same ligands supports the above conclusion and confirms that the luminescence of the Pt(II) complexes is mainly MLCT in nature and that of the Pt(IV) complexes is essentially LC.

The lack of luminescence at room temperature suggests that distorted MC excited states can be populated *via* a thermally activated radiationless transition. Such MC levels are expected to lie at lower energies than in the analogous Pt(II) complexes because of the lower ligand-field strength of Pd(II). This is in agreement with the presence and absence of room-temperature luminescence for $Pt(thpy)_2$ and $Pd(thpy)_2$, respectively.

Electrochemistry. The previously studied cyclometalated complexes exhibit irreversible oxidation, presumably involving the metal, and reversible one-electron reduction processes, associated with the cyclometalated ligands. $Pd(Phpy)_2$ and $Pd(Thpy)_2$ follow this usual behavior, but $Pd(bhq)_2$ exhibits irreversible reduction, which implies that the entering electron resides on the metal. This means that, if the *Koopman* theorem is valid [26], the LUMO of $Pd(bhq)_2$ is essentially a MC orbital. This could be due to the rigid nature of the bhq ligand, which causes steric hindrance and, presumably, longer metal-ligand bond distances compared to $Pd(Phpy)_2$ and $Pd(Thpy)_2$. This would prevent a sufficiently close approach for good interaction between metal and ligand with the following consequences: *i*) the splitting between the d orbitals decreases, thus lowering the energy of the highest-energy (empty) d orbital which may actually be close to, or lower than, the π^* ligand orbital; *ii*) bhq is less affected by coordination than the other two ligands, as it appears from the luminescence spectra and lifetimes *(vide supra)*.

The authors would like to thank Mr. *G. Gubellini* for the drawings and Mr. *V. Cacciari* for technical assistance. This work was supported by the *Italian National Research Council*, the *Ministero della Pubblica Istruzione*, and by the *Swiss National Science Foundation*.

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