# 117. Absorption Spectra and Luminescence Properties of Isomeric Platinum(II) and Palladium(II) Complexes Containing 1,1'-Biphenyldiyl, 2-Phenylpyridine, and 2,2'-Bipyridine as Ligands

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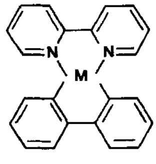
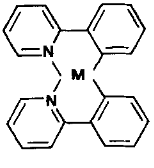
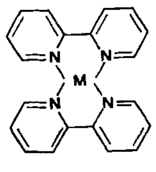
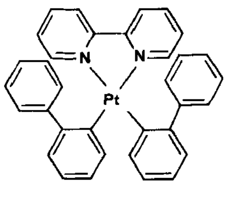
The absorption spectra, luminescence spectra, and luminescence lifetimes of the isomeric [M(bph)(bpy)] and [M(phpy)$_2$] complexes (M = Pt(II) or Pd(II), bph$^{2-}$ = 1,1'-biphenyl-2,2'-diyl dianion, phpy$^-$ = 2-phenylpyridine-2'-yl anion, and bpy = 2,2'-bipyridine) have been investigated and compared with those of [M(bpy)$_2$]$^{2+}$ complexes and of the free protonated ligands H$_2$bph, Hbpy$^+$, and Hphpy. In the absorption spectra, the region below 320 nm is dominated by ligand-centered (LC) transitions, whereas metal-to-ligand charge transfer (MLCT) transitions are responsible for the bands present in the near UV/VIS region. The MLCT bands move to higher energies on replacing Pt with Pd and in going from [M(bph)(bpy)] to the [M(phpy)$_2$] isomer. For the mixed-ligand complexes, evidence for both M→bph$^{2-}$ (at higher energies) and M→bpy bands is found. The structured luminescence observed at 77 K shows lifetimes of 4.0 and 1.1 μs for [Pt(phpy)$_2$] and [Pt(bph)(bpy)], respectively, and 480 and 250 μs for the analogous Pd complexes. On the basis of the energy and lifetime data, the luminescence of the Pt(II) complexes is assigned to the lowest triplet MLCT excited state, whereas for the Pd complexes the luminescent state is thought to result from a mixture of MLCT and LC triplet levels.

**Introduction.** – In the last few years, the photochemical and luminescent properties of cyclometalated complexes have been the object of extensive investigation [1–10]. Continuing our studies in this field, we report here results concerning the species [M(bph)(bpy)] (M = Pd and Pt, bph$^{2-}$ = 1,1'-biphenyl-2,2'-diyl dianion, bpy = 2,2'-bipyridine) which are interesting isomers of the previously studied [1] [4] [M(phpy)$_2$] (phpy$^-$ = 2-phenylpyridine-2'-yl anion) complexes. For comparison purposes, the properties of [Pt(Hbph)$_2$(bpy)] (Hbph$^-$ = 1,1'-biphenyl-2-yl anion), and of the free protonated H$_2$bph, Hphpy, and Hbpy$^+$ ligands are also reported.


[M(bph)(bpy)]


[M(phpy)$_2$]


[M(bpy)$_2$]$^{2+}$


[Pt(H$_2$bph)$_2$(bpy)]

**Experimental.** – The preparation, purification, and characterization of [Pd(bph)(bpy)] [11], [Pt(bph)(bpy)] [11], [*c*-Pd(phpy)$_2$] [12], [*c*-Pt(phpy)$_2$] [13], [Pd(bpy)$_2$(PF$_6$)$_2$] [14], [Pt(bpy)$_2$(PF$_6$)$_2$] [15], and [Pt(Hbph)$_2$(bpy)] [11] have been previously reported. MeCN and $CH_2Cl_2$ (spectroscopic grade), and freshly distilled butyronitrile were used as solvents. The absorption spectra were recorded with a *Kontron-Uvicon 860* spectrophotometer. Emission spectra (uncorrected) were obtained with a *Perkin-Elmer LS5* spectrofluorimeter equipped with a *Hamamatsu R 928* phototube. Emission lifetimes were measured with a *JK* system *2000 Neodymium YAG DLPY4* laser ($\lambda_{exc}$ = 355 nm, pulse half-width 25 ns).

**Results.** – The complexes examined were thermally stable in the solvents used during the time periods of the experiments. The absorption spectra in MeCN of [M(bph)(bpy)], [M(phpy)$_2$], and [M(bpy)$_2$] in MeCN solution at room temperature are reported in *Figs. 1–3* together with the spectra of the free protonated ligands. The frequency and

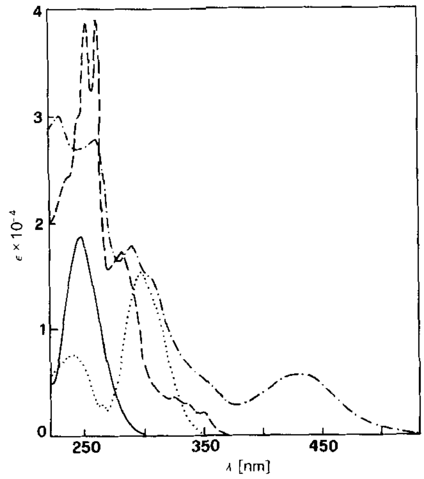


Fig. 1. *Absorption spectra of [Pd(bph)(bpy)]* (– – –), *[Pt(bph)(bpy)]* (–·–·–), *$H_2$bph* (——), *and Hbpy$^+$* (····) *in MeCN at r.t.*

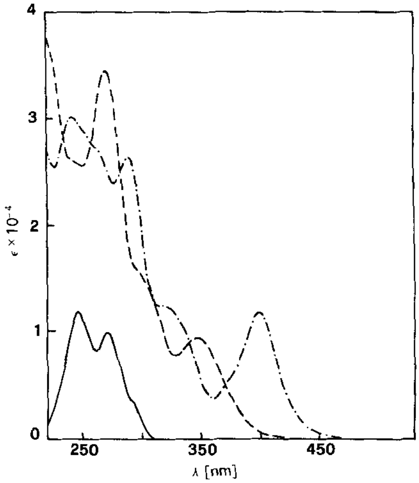


Fig. 2. *Absorption spectra of [Pd(phpy)$_2$]* (– – –), *[Pt(phpy)$_2$]* (–·–·–), *and Hphpy* (——) *in MeCN at r.t.*

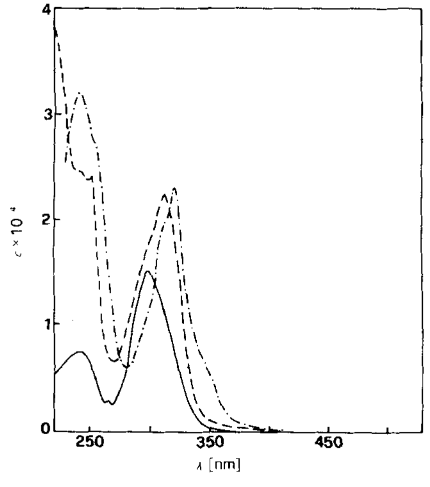


Fig. 3. *Absorption spectra of [Pd(bpy)$_2$]$^{2+}$* (– – –), *[Pt(bpy)$_2$]$^{2+}$* (–·–·–), *and Hbpy$^+$* (——) *in MeCN at r.t.*

Table. *Absorption and Emission Data for the Pt(II) and Pd(II) Cyclometalated Complexes and Model Compounds*

| | Absorption[a]) | | Emission[b]) | |
|---|---|---|---|---|
| | $\nu$[c]) [$cm^{-1}$] | $\varepsilon$ | $\nu$[d]) [$cm^{-1}$] | $\tau$[e]) [µs] |
| [$Pd(phpy)_2$] | 28900 | 9500 | 21800 | 480 |
| [Pd(bph)(bpy)] | 28650 | 2200 | 21140 | 250 |
| [$Pd(bpy)_2$]$^{2+}$ | 32050 | 22400 | | |
| [$Pt(phpy)_2$] | 25100 | 11900 | 20400 | 4.0 |
| [Pt(bph)(bpy)] | 23300 | 5700 | 17200 | 1.1 |
| [$Pt(bpy)_2$]$^{2+}$ | 31060 | 23000 | 22000 | 24.0 |
| [$Pt(Hbph)_2(bpy)$] | 22600 | 1000 | 18940 | 5.7 |
| [Hphpy] | 36500 | 9800 | 23300 | $> 1 \times 10^5$ |
| [$H_2bph$] | 40300 | 18800 | 23050 | $> 1 \times 10^5$ |
| [Hbpy]$^+$ | 33100[f]) | 14700[f]) | 22950[g]) | $1.0 \times 10^6$[h]) |

[a]) MeCN soln. at 293 K, unless otherwise noted.

[b]) Butyronitrile soln. at 77 K, unless otherwise noted.

[c]) Only the maximum of the lowest energy absorption band is reported: for full spectra, see *Figs. 1–3*.

[d]) Highest energy feature of the phosphorescence emission.

[e]) Estimated error ±10%.

[f]) $1.25 \times 10^{-2}$ M HCl (F. H. Westheimer, O. T. Benfey, *J. Am. Chem. Soc.* **1956,** *78,* 5309).

[g]) $MeOH/H_2SO_4$ (see [18]).

[h]) Ethyleneglycol/$H_2O$ 1:1 (J. E. Hillis, M. K. DeArmond, *J. Lumin.* **1971,** *4,* 273).

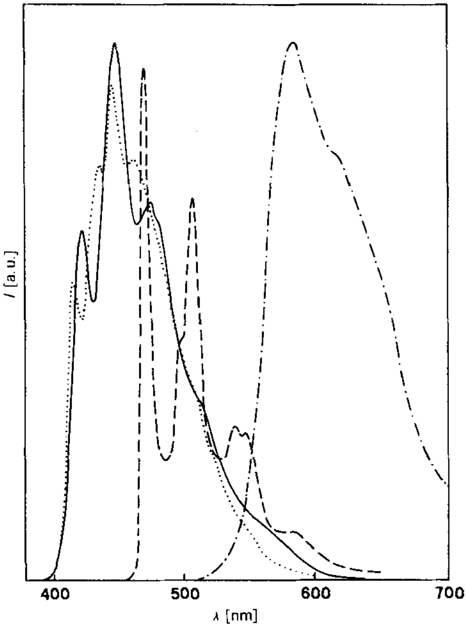


Fig. 4. *Emission spectra of [Pd(bph)(bpy)]* (– – –), *[Pt(bph)(bpy)]* (–·–·–), *$H_2bph$* (——), *and Hbpy$^+$* (· · · ·) *in butyronitrile at 77 K*

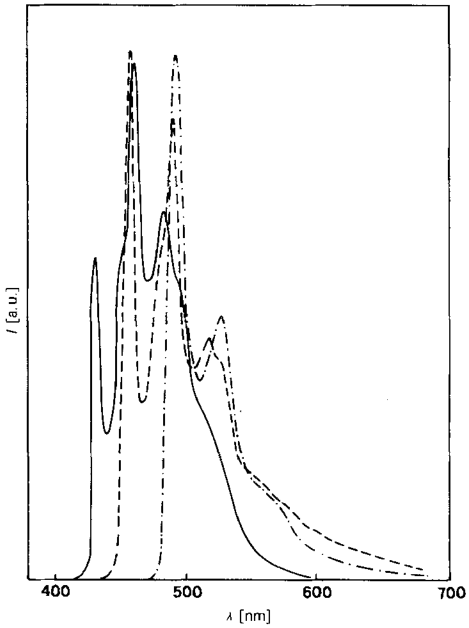


Fig. 5. *Emission spectra of [Pd(phpy)$_2$]* (– – –), *[Pt(phpy)$_2$]* (–·–·–), *and Hphpy* (——) *in butyronitrile at 77 K*

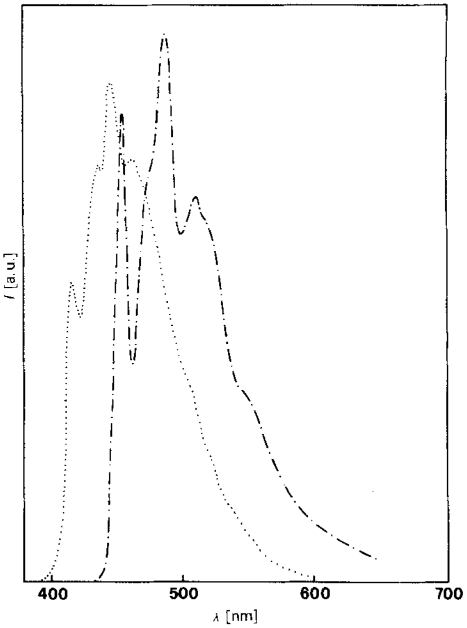


Fig. 6. *Emission spectra of* $[Pt(bpy)_2]^{2+}$ *(–––), and* $Hbpy^+$ *(· · · ·) in butyronitrile at 77 K*

extinction coefficient of the maximum of the lowest-energy band of the various complexes (including $[Pt(Hbpy)_2(bpy)]$) is given in the *Table*. The absorption spectra were found to be solvent dependent, as previously reported [8].

The luminescence spectra of [M(bph)(bpy)], $[M(phpy)_2]$, and $[Pt(bpy)_2]^{2+}$ and of the correspondent ligands in butyronitrile at 77 K are shown in *Figs. 4–6*. In butyronitrile or MeOH/EtOH solutions, $[Pd(bpy)_2]^{2+}$ is labile. In MeCN, which gives a bad matrix, no emission has been observed. The emission spectrum of $[Pt(Hbph)_2(bpy)]$ is quite similar to that of [Pt(bph)(bpy)] but blue shifted by ~ 1700 $cm^{-1}$. The emission maxima are gathered in the *Table* where also the emission lifetimes in butyronitrile at 77 K are reported. The relative luminescence quantum yields in butyronitrile at 77 K were: 1 ($[Pt(phpy)_2]$), 0.4 ($[Pt(bpy)_2]^{2+}$), 0.2 ([Pd(bph)(bpy)], and [Pt(bph)(bpy)] and [Pt(bph)(bpy)]), and ~ $10^{-3}$ ($[Pd(phpy)_2]$). A comparison with the luminescence emission of $[Pd(phpy)_2]$ in a different solvent indicates that the absolute quantum yield of $[Pt(phpy)_2]$ is of the order of unity.

**Discussion.** – For the sake of simplicity, we discuss the spectroscopic properties of the complexes examined in the frame of the 'localized molecular orbital configuration' approach [16] [17]. In such an approach, the various spectroscopic transitions (and excited states) are classified as metal-centered (MC), ligand-centered (LC), and charge-transfer (CT). For complexes of metals in low oxidation states, like Pd(II) and Pt(II), only MLCT transitions (and excited states) need to be considered.

*Absorption Spectra.* Because of solubility reasons, only diluted ($< 1 \times 10^{-3}$ M) solutions could be studied so that only high intensity bands ($\varepsilon > 1000$ $M^{-1}$ $cm^{-1}$) were recorded. This generally precludes the observation of MC bands.

As one can see from *Figs. 1–3*, the spectral region below 320 nm is dominated by bands which are similar to those exhibited by the ligands and that can, thus, be assigned to more or less metal perturbed LC transitions. For the $[M(phpy)_2]$ complexes such bands are somewhat solvent-dependent, in agreement with a partial (intra-ligand) CT character of the LC transitions caused by the fact that the ligand is made by two different aromatic rings [4]. While the $[M(bpy)_2]^{2+}$ complexes do not show appreciable absorption features above 320 nm (with the exception of a shoulder at ~ 350 nm for $[Pt(bpy)_2]^{2+}$), the spectra of the cyclometalated complexes exhibit distinct absorption bands in the 350–450-nm region with extinction coefficients of the order of $10^4$ $\text{M}^{-1} \cdot \text{cm}^{-1}$. In the frame of the localized MO configuration approach, such bands can be assigned to MLCT transitions. As noted previously [1] [11], this assignment is consistent with the marked solvent dependence of the bands and with their disappearance (for the Pt complexes) on oxidative addition [2]. *Figs. 1* and *2* show that the MLCT bands move to higher energy in going from Pt to Pd, as is usually the case in cyclometalated complexes [4].

In the $[M(bpy)_2]^{2+}$ complexes, the MLCT bands are apparently hidden below the LC bands at $\lambda < 350$ nm. Such a blue-shift compared with the spectra of the $[M(phpy)_2]$ and [M(bhp)(bpy)] complexes was expected, because the metal brings a more positive charge in the $[M(bpy)_2]^{2+}$ species. In $[M(phpy)_2]$, the less positive charge of the metal is only partially counterbalanced by the fact that $phpy^-$ is more difficult to reduce than bpy [5]. The further red-shift observed for [M(bph)(bpy)] compared to $[M(phpy)_2]$ is due to the presence of bpy in the latter complex.

The $[M(phpy)_2]$ complexes apparently exhibit only one MLCT band, whereas the isomeric mixed-ligand [M(bph)(bpy)] complexes exhibit absorption features constituted by more than one band. As previously noted [11], in [Pt(bph)(bpy)] the maximum at 429 nm and the shoulder at ~ 350 nm in MeCN solution move to 441 and ~ 330 nm, respectively, in $CH_2Cl_2$, indicating that they correspond to CT transition involving the two different ligands [11].

*Luminescence.* As shown in *Figs. 4–6* and the *Table*, the three protonated ligands exhibit a structured long-lived luminescence in butyronitrile at 77 K, typical of the lowest triplet of aromatic molecules. These spectra are quite similar in energy and structure, as expected because of the similarity of the molecules.

The lack of luminescence for $[Pd(bpy)_2]^{2+}$ is likely due to the fact that the lowest excited state is a distorted MC excited state which undergoes fast radiationless decay. All the remaining complexes exhibit a more or less structured emission, indicating that the lowest excited state is either MLCT or LC (in the frame of a localized MO-configuration approach). The relatively long luminescence lifetimes *(Table)* indicate that, as expected, the emitting excited state is, formally, a triplet. The lack of emission at room temperature suggests that increasing temperature opens efficient deactivation channels most likely related to the presence of thermally accessible MC excited states, as is known to be the case for other Pd(II), Pt(II), and Rh(III) cyclometalated complexes [6].

The assignment of the observed emissions to either LC or MLCT excited states poses some problems, especially for the Pd compounds. Distinction between LC and MLCT emission is usually based on the following criteria:

*i) Energy.* LC emission is only slightly red-shifted from the emission of the corresponding free protonated ligand. A strong red shift can be taken as evidence for MLCT emission.

*ii) Lifetime.* LC emission is less sensitive to the presence of the (heavy) metal atom than MLCT emission. Thus, the longer is the radiative lifetime, the purer is the LC character of the emitting excited state.

*iii) Band Structure.* A LC excited state is more distorted (on the ligand) than a MLCT excited state, because in the former case an electron is transferred from a $\pi$ bonding to a $\pi^*$ antibonding orbital, whereas in the latter the electron promoted to the $\pi^*$ orbital comes from a (nonbonding) d metal orbital. One can, thus, expect that the intensity distribution is more and more concentrated towards the zero-zero vibrational transition with increasing MLCT character. For MLCT transitions, involvement of medium frequency M–L vibrations is also expected to lead to a less resolved vibrational structure.

*iv) Solvent Dependence.* The MLCT transitions cause a change in the dipole moment of the molecule. As a consequence, the energy of MLCT emission (as well as absorption) is expected to depend on solvent polarity, whereas LC transitions (at least in symmetric ligands) are expected to be less influenced by the solvent. It should be noted, however, that the solvent effects may be small in rigid matrix at 77 K for obvious reasons.

On the basis of the above criteria, the $[Pt(bpy)_2]^{2+}$ luminescence *(Fig. 6)* can clearly be assigned to a LC transition. The red shift from the emission of the free ligand is only 950 $cm^{-1}$ (for comparison, 600 $cm^{-1}$ for $[Rh(bpy)_3]^{3+}$ [18]), the radiative lifetime ( $\sim 10^{-4}$ s) longer than that of other Pt(II) complexes, and the band structure is quite similar to that of the free bpy.

Using the same criteria, the $[Pt(phpy)_2]$ [1] and $[Pd(phpy)_2$ [4] emissions were previously assigned as MLCT and LC, respectively. In both cases, however, it was observed that such a classification was not fully satisfactory, and that some LC/MLCT mixing should be taken into consideration.

For [Pd(bph)(bpy)] *(Fig. 4)*, the red-shift from the free-ligand emissions is $\sim$ 1900 $cm^{-1}$, the radiative lifetime is about $10^{-3}$ s, and the band structure is different from that of the free ligands but still well resolved. This situation does not allow a clear-cut assignment, and one should again invoke a LC-MLCT mixture.

For [Pt(bph)(bpy)] *(Fig. 4)* and $[Pt(Hbph)_2(bpy)]$ *(Table)* the situation is much clearer. The red-shift from free ligand emissions is *ca.* 6000 $cm^{-1}$ and 4000 $cm^{-1}$, respectively, the radiative lifetime is of the order of $10^{-5}$ s, and the band structure is quite different from the free-ligand emissions. Thus, one can confidently assign their luminescence to MLCT excited states.

Finally, it is quite interesting to compare the data concerning each $[M(phpy)_2]$/[M(bph)(bpy)] couple. For M = Pt, there is clearly a strong displacement ( $\sim$ 3200 $cm^{-1}$) towards lower energies of the luminescent band, as expected for MLCT emitting levels, because bpy is easier to reduce than phpy [5]. Interestingly, this shift is much larger than that observed for the maximum of the absorption bands (*Figs. 1* and *2*). This suggests that the broad absorption feature of [Pt(bph)(bpy)] with maximum at 429 nm in MeCN is the result of overlapping bands. By contrast, the luminescence of [Pd(bph)(bpy)] is quite similar in energy, lifetime, and structure to the $[Pd(phpy)_2]$ emission, as expected for LC emissions from ligands with similar structures.

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