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LUMINESCENCE PROPERTIES OF TWO NEW Pt(II)-2-PHENYLPYRIDINE COMPLEXES; THE INFLUENCE OF METAL-CARBON BONDS

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SUMMARY

Preparations and characterizations of two novel Pt(II) organometallic complexes, each containing the ortho-metalating ligand 2-phenylpyridine (ppy$^-$) are reported. One of the complexes, $[Pt(ppy)(Cl)_2]^{1-}$, is anionic. A second complex, [Pt(ppy)(H-ppy)Cl], is neutral and contains one ortho-metalated 2-phenylpyridine and one N-coordinated monodentate 2-phenylpyridine ligand (H-ppy). These two complexes were characterized by both ^1H and ^{13}C NMR. Photophysical investigations reveal that the lowest energy excited states of both complexes are metal-to-ligand charge-transfer states. The anionic Pt(II) complex is luminescent at room temperature as a solid, although no luminescence is detected at room temperature in fluid solution. In addition, a low energy transition is observed in the excitation spectra of this solid and the transition is indicative of a band-gap type absorption. The neutral Pt(II) complex luminesces in fluid solution at room temperature from a long-lived excited state. The magnitude of the luminescence lifetime for this complex is solvent dependent with observed room temperature lifetimes ranging from 677 ns in ethanol to 5.9 µs in dichloromethane.

INTRODUCTION

Photosensitizers are of interest in solar energy conversion schemes as a means of utilizing visible light to drive electron transfer or energy transfer reactions. Ortho-metalated Pt(II) complexes have been of interest recently because of their light absorbing and light emitting properties (ref. 1). We have been investigating transition metal organometallic complexes in order to evaluate them as photosensitizers or photoredox catalysts. Transition metal complexes that are bound to ortho-metalating ligands are particularly interesting because of the characteristics that these ligands impart to the complex (ref. 2,3). We have recently prepared and characterized two new Pt(II) complexes

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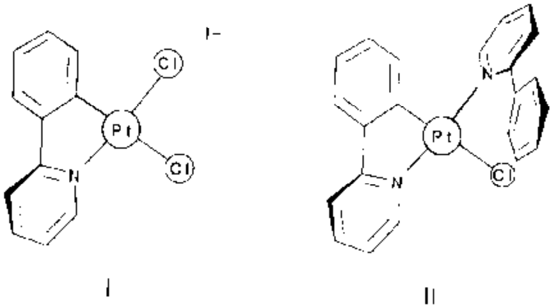
with metallated 2-phenylpyridine (ppy$^-$).

2-Phenylpyridine has been shown to bind in a bidentate fashion forming ortho-metalated complexes with transition metals such as Ir(III) (ref. 3-8), Rh(III) (ref. 3,4,9-13), Os(II) (ref. 14), Ru(II) (ref. 15,16), Pd(II) (ref. 17-20) and Pt(II) (ref.21-24). It has been argued that addition of electron density to the transition metal center through the deprotonated, formally anionic carbon of this ortho-metalating ligand lowers the energy of metal-to-ligand charge-transfer (MLCT) transitions to pi-acceptor ligands that share the coordination sphere of the metal center (ref. 2,3). This factor can be used in the design of complexes that absorb photons in the visible spectral region. Knowledge of structural effects on both the energies and lifetimes of excited states are important in the development of photosensitizers. In this work, we have studied the effects on these parameters of two modes of binding of the ligand, 2-phenylpyridine, to Pt(II). The two Pt(II) complexes which were prepared and characterized, [Pt(ppy)(Cl)$_2$]$^{1-}$, (I) and [Pt(ppy)(H-ppy)Cl], (II) are illustrated in **Figure 1.**



I

II

Fig. 1. Illustration of modes of binding of 2-phenylpyridine to Pt(II) in [Pt(ppy)(Cl)$_2$]$^{1-}$ and in [Pt(ppy)(H-ppy)Cl].

METHODS

Syntheses

Tetrabutylammonium-dichloro (2-phenylpyridine-C^2,N$'$) platinate(II): (Bu$_4$N)$_2$[PtCl$_4$] was prepared by a phase-transfer metathesis reaction by mixing 0.8 g (1.9 mmol) of K$_2$[PtCl$_4$] (Strem Chemicals) in water with 0.23 g (8.2 mmol) of (Bu$_4$N)Cl (Aldrich) in CH_2Cl_2. The organic phase containing $(Bu_4N)[PtCl_4]$ was passed through filter paper to remove residual water. 1.2 g (7.9 mmol) of 2-phenylpyridine (Aldrich) in 50 mL of methanol was added to the CH_2Cl_2 solution containing $(Bu_4N)_2[PtCl_4]$. The solution was warmed to 50°C and kept at this temperature until yellow-green, shiny crystals appeared. The reaction solution was then cooled to ambient temperature. Additional yellow-green crystals were formed on the addition of diethylether. The crystals were washed with diethylether and air dried (28% yield). This complex is stable in dichloromethane; however, rapid thermal reaction in acetonitrile was observed.

Anal. Calcd. for $PtC_{27}H_{44}N_2Cl_2$: C, 48.94; H, 6.69; N, 4.23; Pt, 29.44; Cl, 10.70

Found: C, 48.73; H, 6.60; N, 4.24; Pt, 28.23; Cl, 10.55

Chloro-(2-phenylpyridine-N$'$)(2-phenylpyridine-C^2,N$'$)platinum(II): Dichloro(1,5-cyclooctadiene)platinum(II) (0.1234 g, Strem) was dissolved in 175 mL of 95% ethanol and heated at 40 °C for 1 hour. Sodium acetate (approx 200 mg) and a fourfold excess of 2-phenylpyridine (H-ppy) were added to the flask and the reaction was stirred for 48 h at ambient temperature. The solution was then heated slightly with a flow of nitrogen over the solution to allow complete evaporation of the solvent. A yellow solid was removed from the reaction flask and washed with hexanes. Excess 2-phenylpyridine was removed by dissolving the washed reaction product in dichloromethane and extracting $[H\text{-}ppyH]^+$ in dilute HCl. The dichloromethane was then evaporated and the remaining solid washed with water and hexanes yielding 0.1164 g (59% yield) of [Pt(ppy)(H-ppy)Cl].

Anal. Calcd. for $PtC_{22}H_{17}N_2Cl$ $3/4CH_2Cl_2$: C, 45.10; H, 3.08; N, 4.64.

Found: C, 45.56; H, 3.14; N, 4.41.

Measurements

The instrumentation used to obtain absorption, emission and luminescence lifetime data is described elsewhere (ref. 25). Solid sample luminescence data were collected with the neat powder pressed between quartz plates and placed in the path of the incident radiation with emitted light observed at 90° to incident off the back surface of the quartz plates to minimize interference from scattered light. Low-temperature glasses were all prepared using Burdick & Jackson high-purity solvents, which were found to be suitable for spectroscopic studies without further purification. Low-temperature glasses were prepared from a 2:1 by volume ratio of n-propanol:pentane. For each low-temperature glass sample, approximately 5 mg the platinum complex was dissolved in 3 mL of dichloromethane and then added to 30 mL of the n-propanol:pentane solution in a quartz sample tube. The sample tube was then immediately immersed in liquid nitrogen, forming a lightly colored glass suitable for spectroscopic investigation. ^{1}H NMR and ^{13}C NMR spectra were obtained on a GN-500 FT NMR. The excitation spectra described here were obtained by observing emission intensities at 550 nm.

RESULTS AND DISCUSSION

Compound Characterizations

TABLE 1

^{1}H NMR chemical shift data for $[Pt(ppy)(Cl)_2]^{1-}$ and $[Pt(ppy)(H-ppy)Cl]$

$[Pt(ppy)(Cl)_2]^{1-}$ [a]			$[Pt(ppy)(H-ppy)Cl]$[b]		
d ppm	(mult)[c]	integ	d ppm	(mult)[c]	integ
9.88	D	1	9.65	D	1
8.00	D	1	9.25	D	1
7.80	DD	1	8.10	M	2
7.58	D	1	7.95	DD	1
7.36	D	1	7.75	DD	1
7.05	M	3	7.65	D	1
			7.54	D	1
			7.42	M	1
			7.35	M	4
			7.05	DD	1
			7.00	DD	1
			6.88	DD	1
			6.20	D	1

[a] in CD_2Cl_2
[b] in $CDCl_3$
[c] D=doublet,DD=doublet-of-doublets and M=multiplet.

The ortho-metalated Pt(II) complex $(bu_4N)[Pt(ppy)(Cl)_2]$ was characterized by ^{1}H NMR and ^{13}C NMR. The proton NMR spectrum for

I has six chemical shifts (see Table 1) in the aromatic region of the spectrum. Four well resolved doublets, each integrating for a single proton, are observed in the ^1H NMR spectrum. Only one doublet of doublets integrating for a single proton is observed. The remaining chemical shifts can be observed as a multiplet at 7.05 ppm, integrating for three protons. The total integration of the aromatic region of the spectrum shows eight protons, indicating a deprotonated 2-phenylpyridine ligand in which one proton has been displaced from (H-ppy) as a result of carbon-metal bond formation. The counter ion for complex I, tetrabutylammonium, exhibits four chemical shifts in the aliphatic region of the ^1H NMR spectrum.

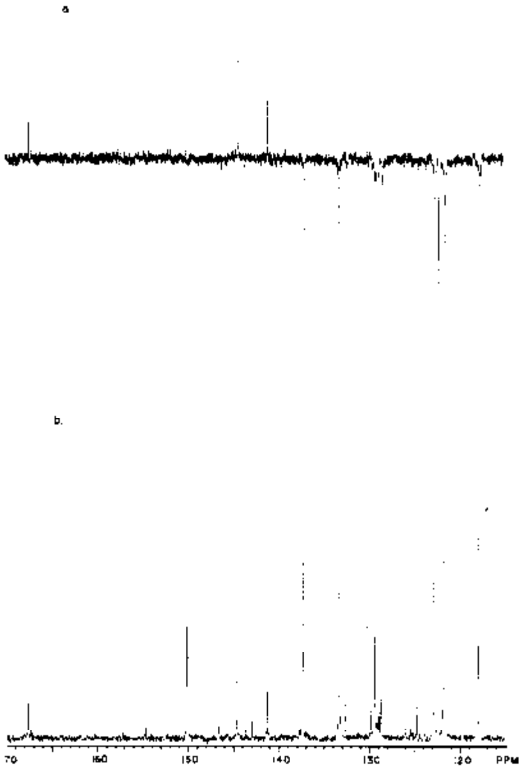


Fig. 2. ^{13}C APT NMR (a) and ^{13}C NMR (b) of $[Pt(ppy)(Cl)_2]^{1-}$ in CD_2Cl_2.

^{13}C proton decoupled and ^{13}C attached proton test (APT) NMR spectra of complex I are presented in **Figure 2**. The ^{13}C NMR shows 11 low-field resonances of ppy^- between 118 and 168 ppm, corresponding to 11 carbon atoms of the aromatic ligand. The ^{13}C APT spectrum clearly illustrates the presence of 10 resonances. The seven highest field resonances (118-138 ppm) are inverted, indicating methine or methyl carbon atoms. Three resonances, located at 141.3, 144.6, and 167.8 ppm, remain upright corresponding to quaternary or methylene carbon atoms. This confirms the presence of two bridging carbon atoms and one ortho-metalated carbon on the ppy^- ligand. One signal is not present in the APT spectrum. The resonance at 150.0 ppm is suppressed as a result of a 90° phase shift (ref. 26). The high-field (aliphatic) region of the ^{13}C NMR spectrum does show four resonances for the butyl carbons of the tetrabutylammonium counter ion. The positions of these chemical shifts are 59.5, 24.5, 20.0, and 13.5 ppm. The elemental analysis and NMR spectral data confirm the identity of an anionic Pt(II) complex containing an ortho-metalated ppy^- ligand and two chloride ligands.

^1H NMR spectroscopy was utilized to characterize complex II, [Pt(ppy)(H-ppy)Cl]. Elemental analysis suggests that complex II is a platinum monomer containing two 2-phenylpyridine ligands. The number of chloride ligands cannot be unambiguously determined from the analysis due to the presence of dichloromethane in the lattice of recrystallization. The ^1H NMR spectrum of II is complicated, displaying 13 chemical shifts in the aromatic region of the spectrum between 6.0 and 10.0 ppm. Chemical shifts with their positions and multiplicities are listed in Table 1. The complexity of the ^1H NMR spectrum indicates that the two 2-phenylpyridine ligands are not magnetically equivalent. A *cis* or a *trans* dichloride complex of Pt(II) with two N-coordinated 2-phenylpyridine ligands would most likely be symmetric and would have chemically equivalent 2-phenylpyridine ligands in solution. Therefore, the possibility of a Pt(II) complex with two chloride ligands can be discounted. Integration of the aromatic region of the proton spectrum indicates that 17 protons are present. Two monodentate, N-coordinated, H-ppy ligands would have 18 protons, whereas two ortho-metalated ppy^- ligands would have only 16 protons in the aromatic region of the spectrum. This information suggests that one of the 2-phenylpyridine ligands bound to Pt(II) is ortho-metalated, with a second N-coordinated but not metallated ligand also bound to the metal center.

The presence of a doublet resonance integrating for a single proton at very high field, 6.2 ppm, is indicative of a proton adjacent to a metalated carbon atom (ref 9,20). Furthermore, the position of this high-field chemical shift (6.2 ppm) suggests that the proton adjacent to the ortho-metalated carbon atom is pointing directly toward the aromatic ring (ref. 27), which shields this proton. This situation would occur in complex II if the N-coordinated H-ppy ligand were bound cis to the carbon-metal bond of the ortho-metalated ligand and were in a perpendicular or near-perpendicular position relative to the plane created by the ppy^- ligand and the metal atom. Previous crystal structure results for a similar Pt(II) ortho-metalated complex (ref. 28) support this possibility.

There are two doublet resonances each integrating for one proton in the low-field region of the ^1H NMR spectrum (9.2-9.7 ppm) of complex II. Doublets seen in the low-field region for similar complexes have been assigned to protons adjacent to coordinated aromatic nitrogen atoms (ref. 17,20,22). Again this suggests that there are two magnetically unique 2-phenylpyridine ligands bound to the Pt(II) center. Integration of the ^1H NMR spectrum and evidence for the presence of two distinct 2-phenylpyridine moieties confirms that complex II is a platinum complex containing one ortho-metalated (ppy^-) ligand, one N-coordinated (H-ppy) ligand, and one chloride ligand.

There are two possible conformations of II: one with the chloride cis to the coordinated pyridyl ring of the ortho-metalated ppy and one with chloride cis to the metallated phenyl ring. The X-ray crystallographic structure of a very similar complex of Pt(II) (ref. 28), where the ligands are 2-(2′-thienyl)pyridine showed that the monodentate, N-coordinated ligand was bound cis to the metallated ring of the ortho-metalated ligand. The N-coordinated ligand was also found to have the free ring near the axial position of the complex. This forces the proton adjacent to the metalated carbon atom to point toward the center of the pyridyl ring. Therefore, the interpretation of the ^1H NMR and the assignment of the high-field resonance in complex II (vida supra) supports a similar structure to that of the 2-(2′-thienyl)pyridine Pt(II) complex.

Ultraviolet/Visible Spectra

The Ultraviolet/Visible absorption spectra for complexes I and II are shown in **Figure 3**. Both I and II have high-energy absorption features (see Table 2). The 2-phenylpyridine ligand (H-ppy) shows ultraviolet absorption transitions (λ < 300 nm) that are characteristic of pi-pi* ligand localized transitions (ref.17,24). Complexation of 2-phenylpyridine to a transition metal causes some perturbation of the ligand molecular orbitals. In some cases, the ligand-localized transitions occur at energies as low as 360 nm (ref.17). Absorption transitions at wavelengths greater than 370 nm in transition metal complexes bound by (ppy$^-$) are not ligand-localized 2-phenylpyridine transitions. These visible transitions are usually assigned on the basis of position and intensity as MLCT transitions. Optical transition energies and extinction coefficients for several ortho-metalated Pt(II)-2-phenylpyridine complexes are compiled in Table 2.

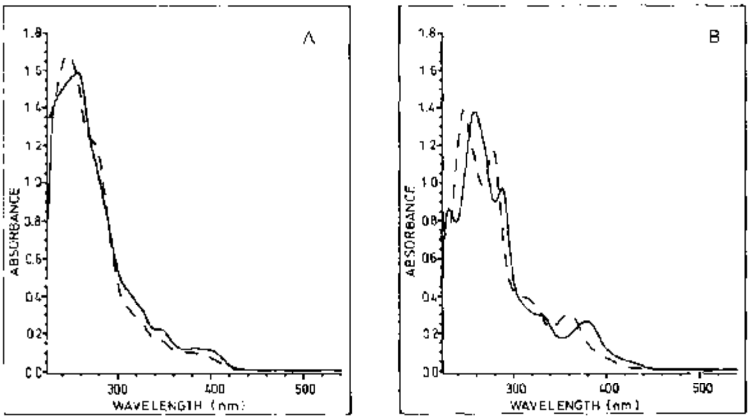


Fig.3. Ultraviolet/visible absorption spectra of $[Pt(ppy)(Cl)_2]^{1-}$ (a) and [Pt(ppy)(H-ppy)Cl] (b) in CH_2Cl_2(——) and ethanol(- - -)

TABLE 2

Absorption energy maxima and extinction coefficients for several Pt(II)-2-phenylpyridine complexes in CH_2Cl_2

Compound	Absorption Features (nm)	Extinction Coefficient 10^{-3} M^{-1} cm^{-1}
$(bu_4N)[Pt(ppy)(Cl)_2]$	257	23
	287	17
	379	4.4
	488	0.061
[Pt(ppy)(H-ppy)Cl]	260	14
	348	1.9
	404	0.8
$[Pt(ppy)_2]$[a]	376	5.4
	402	10.4
	484	0.090

[a] Data from Chassot and von Zelewsky

Complex I shows a very large solvatochromic shift. The visible transitions are shifted by as much as 20 nm to higher energy in ethanol relative to dichloromethane. The UV transitions (< 370nm) are also shifted to higher energy in more polar solvents but the magnitude of the shift is slightly less than that observed for the visible transitions. Solvatochromism is indicative of a large change in the polarity of the excited state of the molecule relative to the ground state. This is usually the case for charge-transfer transitions (ref.29-31). The magnitude of the shifts observed for complex I are very large while those seen for complex II are somewhat smaller. Based on the energies of the visible transitions for I and II together with the observation of solvatochromism for each, we assign the visible absorption bands (370-450 nm) as MLCT bands. A single, low-intensity electronic transition is observed for I at 488 nm. A low-energy band has also been reported for $[Pt(ppy)_2]$ at 484 nm (ref.23) and was assigned as a triplet MLCT transition. The absorption band at 488 nm for I is assigned as a spin forbidden triplet charge-transfer transition on the basis of its similarity to the 484 nm band of $[Pt(ppy)_2]$.

The energies of MLCT transitions of ortho-metalated complexes may be lowered relative to those of similar coordination complexes by the strong sigma-donor effects of the metallating ligand. There is an interesting observation that can be made by comparing the absorption spectra of I and II. The singlet MLCT bands are ca. 20 nm higher in energy for I vs. II in dichloromethane. One explanation for this result is that the electron-accepting ability of the N-coordinated (H-ppy) ligand in complex II in conjunction with the sigma-donor ability of the ortho-metalated ppy^- ligand lowers the energy of the MLCT state. The lack of the H-ppy pi-acceptor ligand in I results in relatively high-energy singlet charge-transfer transitions. Additionally, the energies of the singlet MLCT electronic transitions of [Pt(ppy)(H-ppy)Cl] are similar to the energies of the singlet MLCT transitions of $[Pt(ppy)_2]$ (ref.24). This indicates that for $[Pt(ppy)_2]$, the second electron-donating carbanion does not have as large an effect on the optical transition energies of the complex as the coordination of a good pi-acceptor ligand such as (H-ppy) in the same coordination sphere as the ortho-metalated ligand. This further indicates the importance of having both good electron-donor ligands and good electron-acceptor ligands bound to the same metal center to promote low energy MLCT transitions.

Luminescence Spectra

Luminescence studies of I and II have produced several interesting results. Complex I luminesces both at room temperature and at 77K in the solid state, whereas in fluid solution no luminescence is detected. If a fluid solution of I is used to prepare a glassy matrix at 77K, an emission spectrum of similar structure but at higher energy than that of the solid is observed. Emission spectra of the solid $(bu_4N)[Pt(ppy)(Cl)_2]$ sample and the solvated sample in a rigid glass are shown in **Figure 4.** The similarities in the structured emission spectra are apparent, with the solvated emission spectrum shifted to higher energy by 20 nm. The similarity in the shape of the emission profiles suggest similar emitting states for the solid and solvated samples. The structure noted in the emission spectra of I are common to ortho-metalated 2-phenylpyridine complexes (ref.17,24). The room temperature and 77K emission spectra of [Pt(ppy)(H-ppy)Cl] are shown in **Figure 5**. Unlike I, this complex does luminesce in fluid solution at room temperature. The emission spec-

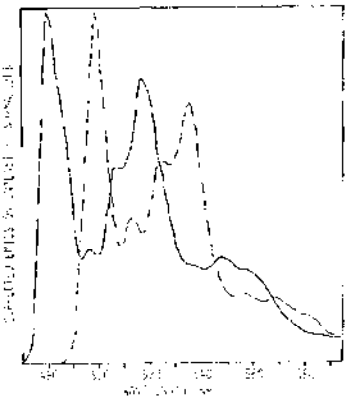


Fig. 4. Emission spectra of $(bu_4N)[Pt(ppy)(Cl)_2]$ at 77 K:(- -), solid; (———), glass solution of *n*-propanol/pentane, 2:1 by volume.

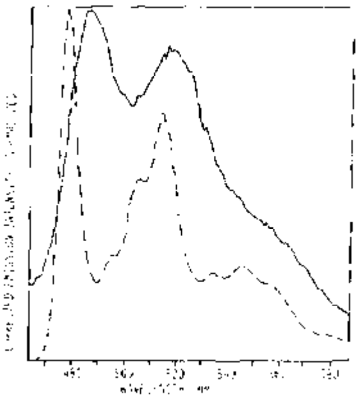


Fig. 5. Emission spectra of {Pt(ppy)(H-ppy)Cl} at 298 K (———) and at 77 K (- - -) in *n*-propanol/pentane (2:1 by volume).

trum is slightly structured at room temperature and becomes highly structured at 77K. Again, the low-temperature emission spectrum of II is characteristic of ortho-metalated 2-phenylpyridine complexes. The λ_{max} values from the emission spectra of I and II at 77K in rigid glasses (see Table 3) are nearly identical. Although the optical transition energies of the singlet MLCT absorption transitions are influenced by electron-acceptor ligand(s) in the Pt(II) coordination sphere, the λ_{max} emission bands are not affected by either overall charge of the metal complex or the presence of electron-acceptor ligands. The λ_{max} of the emission of the homoleptic complex, [Pt(ppy)$_2$], occurs at 491 nm (ref.24), ca. 10 nm lower in energy than for either of the complexes studied here. This indicates that the second metallated (ppy$^-$) ligand influences the energy of the emitting state of square-planer Pt(II) complexes.

TABLE 3

Luminescence data for (bu$_4$N)[Pt(ppy)(Cl)$_2$] and [Pt(ppy)(H-ppy)Cl]

Compound	Lifetime (λmax)			
	Solid 298 K	Solid 77 K	Glass 77 K	Solution 298 K
(bu$_4$N)[Pt(ppy)(Cl)$_2$]	2.8 us (504 nm)	3.6 μs	13.2 μs (498 nm)	____
[Pt(ppy)(H-ppy)Cl]	____	____	14.2 μs (478 nm)	5.9 μs[b] (484 nm) 1.7 μs[c] 677.2 ns[d]

[a] (1:1) by volume n-propanol:pentane glass.
[b] CH$_2$Cl$_2$ solvent.
[c] acetone solvent.
[d] ethanol solvent.

Excitation Spectra

Excitation spectra of (bu$_4$N)[Pt(ppy)(Cl)$_2$] (see **Figure 6**) illustrate an important difference between the solvated sample at 77K and the solid sample at 77K. The excitation spectrum of I, solvated in a rigid glass, displays excitation features similar to those observed in the solution absorption spectrum. The energies of the features are difficult to compare because I has a

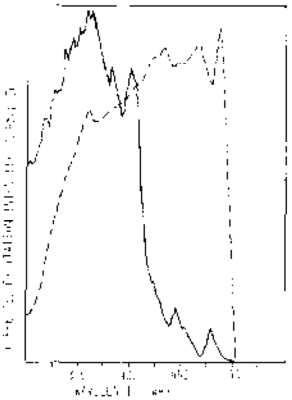


Fig 6. Excitation spectra of $(bu^4N)[Pt(ppy)(Cl)_2]$ at 77 K in n-propanol/pentane (2:1 by volume) glass (———) and as a solid (- - -).

very large solvatochromic shift (vide supra); therefore, the glassy solvent may cause shifts in the energies of the transitions. Substantial absorption occurs at higher energy, however the limits of the instrument prohibit measurement of reliable excitation spectra at wavelengths less than 300 nm. Large differences between the solution-absorption or solvated excitation spectra and the solid state excitation spectrum are evident. The 360 nm feature that dominates the spectrum of the solvated complex is observed as only a shoulder in a much more intense visible transition with a maximum at 500 nm in the solid-state sample. This intense low energy transition is also present in the solid state excitation spectrum of I taken at room temperature. The low-energy edge of these solid-sample excitation spectra do not tail in the manner observed in typical molecular electronic transitions. In fact, the steep falloff of the transition resembles a bandgap-type transition (ref.32). Platinum square-planar complexes have been used in the preparation of stacked linear-chain materials (ref.33), and therefore it is possible that the solid-state excitation feature observed for $(bu_4N)[Pt(ppy)(Cl)_2]$ is a result of solid-state ordering. Additionally, $[Pt(ppy)_2]$ (ref.34) has been reported to form Pt-Pt dimers, which supports the possibility that solid-state stacking may be the reason for the low-energy "bandgap" transition observed in the solid-state excitation spectra of complex I.

Luminescence Lifetimes

Luminescence lifetimes of both I and II are compiled in Table 3. The lifetimes of I and II are characteristic of triplet, charge-transfer excited states (ref.7,24). Ligand-localized triplet-state emissions are typically much longer-lived (ref.17), whereas singlet-fluorescent emissions are much shorter-lived (ref.35,36). This supports the assignment of MLCT emissions for these complexes. Complex I displays very similar lifetimes for both the solid sample at room temperature and at 77K. The solvated complex at 77K has a longer lifetime than the solid at 77K, although the magnitude of the change is not large. This observation suggests that the emitting states are similar for the solid and solvated samples of I. Similarly the lifetime of II at 77K is indicative of a MLCT-emitting state and is very similar to the lifetime of solvated I at 77 K. Room-temperature luminescence lifetimes of II in several solvents are presented in Table 3. There is a significant dependence of the magnitude of the lifetime on the solvent medium, consistent with a MLCT-emitting state for this complex. The lifetime of the excited state of this molecule is extremely long in non-coordinating, low-polarity solvents such as dichloromethane, but decreases in more polar media.

CONCLUSIONS

Characterization of $[Pt(ppy)(Cl)_2]^{1-}$ by ^1H and ^{13}C NMR spectroscopy indicate that it is an ortho-metalated complex of Pt(II). This anionic Pt(II) complex exhibits a very structured emission spectrum in the solid and in a rigid glassy matrix at 77K; however, no luminescence is observed for the complex in fluid solutions at room temperature. The lowest excited state of this complex is characterized as a metal-to-ligand charge-transfer state. The excitation spectrum of this complex in a glassy matrix at 77K matches the absorption features of the complex in fluid solution. However, the solid-state excitation spectrum of I does not corrolate with the solution-absorption spectrum. We attribute the solid-state excitation spectrum to transitions arising from the interactions arising from stacking or ordering in the solid. Several square-planar platinum complexes have been shown to form double-salt complexes (ref.33) or dimers (ref.34) in the solid state. The complex may be of further interest as a precursor for the preparation of double-salt compounds. Complexes of this type are currently under investigation in these laboratories.

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