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Site-Selective Spectroscopy of Luminescent Square-Planar Platinum(II) Complexes

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We report on the site selective luminescence spectroscopy of *trans*-Pt(H)Cl(PEt₃)₂, *trans*-Pt(C≡CH)₂(PEt₃)₂, and *trans*-Pt(C≡CPh)₂(PEt₃)₂. All complexes give intense 77 K emission spectra and have site selective differences in their luminescence properties in a variety of rigid glasses. Depending on precise structure, site sensitivity can be very small to extremely large. The variations in behavior are explained on the basis of the charge-transfer character of the excited state, the environmental volume sampled, and the steric shielding of the excited portion of the complex. Design criteria are established for fabricating complexes that should possess high site selectivity. The parent *cis*-PtCl₂(PEt₃)₂ and *trans*-PtCl₂(PEt₃)₂ complexes are nonluminescent, apparently due to formation of a tetrahedral excited state.

Introduction

There is lively interest in designing transition-metal complexes as environmental messengers,¹ luminescent sensors,² and photo-catalysts.³ Most sensor work has focused on oxygen, but metal complexes have shown sensitivity to environmental polarity,⁴ binding to DNA,⁵ chirality,⁶ and pH.⁷ To date, most work has been done with luminescent octahedral Ru(II), Os(II), and Re(I) complexes⁸ and the dinuclear Pt₂(P₂O₅H₂)₄⁴⁻⁹

As part of our program of designing useful new molecules and examining environmental sensitivity, we have examined the luminescent spectroscopy of square-planar platinum metal complexes. We find that simple hydride and acetylide complexes exhibit complex and interesting site sensitivity of their emission properties. In particular, one acetylide complex exhibits an extraordinarily large site sensitivity with radical changes in its emission properties resulting from modest changes in the excitation wavelength. These results suggest design guidelines for the development of new complexes with high site sensitivity.

Experimental Section

Synthesis. All reactions were performed under dry, prepurified nitrogen. Solvent purification procedures, spectroscopic methods, micro-analytical services, and reagent preparation procedures have been published previously.¹⁰⁻¹³

The complexes studied were *cis*-PtCl₂(PEt₃)₂,¹⁴ *trans*-PtCl₂(PEt₃)₂,¹⁴ *trans*-Pt(H)Cl(PEt₃)₂,¹⁵ *trans*-Pt(C≡CH)₂(PEt₃)₂,¹⁶ and *trans*-Pt(C≡CPh)₂(PEt₃)₂.¹⁶ The references are to the syntheses.

Photophysical Studies. Room-temperature absorption spectra were recorded by using a Hewlett-Packard 8452A diode-array spectrophotometer. Emission and excitation spectra were recorded on a Spex Fluorolog 2 spectrofluorometer. Emission spectra were corrected for solvent background and instrument response, while excitation spectra were only background corrected. Room-temperature emission spectra were measured from deaerated solutions; low-temperature (77 K) spectra were recorded from glass matrices by using an optical Dewar sample holder. Emission spectra of powder samples were recorded using the same 5-mm-diameter quartz cells and sample holder as for the 77 K glass measurements.

The glasses used for the results reported here were isopentane (MEB), 1:1 ether-isopentane (ETOMEB), and 4:1 methanol-water. In addition, we also examined pentane, 5:4 butyronitrile-propionitrile, 100% EtOH, and 100% EtOD.

Luminescence quantum yields, Φ, were measured at low temperature by the Parker-Rees method^{17,18} using [Ru(bpy)₃]Cl₂ (bpy = 2,2'-bipyridine) [Φ = 0.376]¹⁹ as a standard. Measurements of both the standard and the samples were made from 4:1 ethanol-methanol glasses. The quantum yields are the averages of at least two sets of seven measurements with the sample being removed and replaced in the sample holder for every other measurement. Room-temperature absorption spectra were used for sample optical densities, which leads to an estimated ±30% uncertainty on the low-temperature yields.

Excited-state lifetimes (τ) were measured by using a pulsed N₂ laser (337 nm) nanosecond decay system and software described elsewhere.²⁰ The same optical Dewar used for emission spectra was used as the sample holder for the lifetime measurements. The nonexponential decays were

fit by nonlinear least-squares methods²¹ to the sum of two exponentials (eq 1) where *I*(*t*) is the luminescence intensity at time *t* and the *K*'s and

$$I(t) = K_0 \exp(-t/\tau_0) + K_1 \exp(-t/\tau_1) \quad (1)$$

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τ 's are the preexponential weighting factors and the excited-state lifetimes, respectively. The subscripts s and l refer to the short and long-lived components respectively.

Radiative, k_r , and nonradiative, k_{nr} , decay constants and the radiative or intrinsic lifetimes, τ_r , were calculated from

$$k_r = \Phi / \tau \quad (2a)$$

$$k_{nr} = (1 - \Phi) / \tau \quad (2b)$$

$$\tau_r = 1 / k_r \quad (2c)$$

where Φ is the absolute quantum yield and τ is the observed lifetime under the same conditions. τ_r is the lifetime that would be observed if there were no radiationless deactivation of the excited state. These expressions assume that the intersystem crossing efficiency is unity. For a series of platinum metal complexes (Ru(II) and Os(II) with α -diamine ligands), this has been shown to be true.^{3b} Further, it is clear that the intersystem crossing yield for $\text{Pt}_2(\text{pop})_4^{4+}$ is very high since the fluorescence is a minor contribution to the total emission.⁹ Therefore, in the current systems, a unit intersystem crossing yield is a reasonable assumption.

Spectral Decompositions. Many of the emission spectra appeared to be superpositions of two or more emission components, which differ in energy but have the same vibrational structure. We assumed that each emission component had the same spectral shape and differed only in energy. Fitting was done by selecting the simplest observed spectrum and assuming that this represented the common base emission spectrum. We denote this emission spectrum by $E(\bar{\nu})$. The different spectra were fit as a sum of two or more $E(\bar{\nu})$'s centered at different emission energies. Components were obtained by energy shifting the base spectrum. The components were scaled and added together to yield a composite spectrum that matched the experimentally obtained multicomponent emission

$$E(\bar{\nu})_{\text{calc}} = \sum w_i E(\bar{\nu} - \Delta\bar{\nu}_i) \quad (3)$$

where the w 's are the weights for each shifted spectrum and the $\Delta\bar{\nu}$'s are the shifts from the base spectrum. Depending on excitation wavelength, up to 5–10 different spectra were required for a satisfactory fit. Positions and weightings were adjusted manually, and the success was judged by visual comparisons of the fits and from the sums of the squares of the residuals for each generated spectrum. Fits are reported as the relative weights of the different components along with the $\bar{\nu}$ value for the component's highest energy emission maximum.

As a probe of emission heterogeneity, we used the excitation spectra method described earlier.^{20c} For a sample, two uncorrected excitation spectra were measured with different emission wavelengths (λ_1 and λ_2). $R(\lambda)$ is calculated by

$$R(\lambda) = E_1(\lambda) / E_2(\lambda) \quad (4)$$

where the E 's are the emission intensities for exciting at λ and monitoring at two different wavelengths. Since the sample absorbance and excitation intensities are the same at each excitation wavelength, R is related to the relative contributions of different emission components. If there is no ground-state heterogeneity or equilibration in the excited state is rapid relative to the sample decay times, $R(\lambda)$ is wavelength independent. If there are multiple ground species that fail to equilibrate in their excited states, $R(\lambda)$ varies with λ .

This procedure can be used without low-temperature absorption spectra or calibration of the excitation output. It compensates for solvent absorption, is insensitive to solution absorbance, and works with fractured glasses.

Results

Absorption Spectra. *cis*- $\text{PtCl}_2(\text{PEt}_3)_2$ has CH_2Cl_2 solution absorption maxima (ϵ in parentheses) at 244 (7470), 264 (2700), and 320 (900) nm; *trans*- $\text{PtCl}_2(\text{PEt}_3)_2$ shows maxima at 250 (12400), 270 (12050) and 306 (2650) nm. Similar features are observed from ethanol and ether/isopentane solvents. These absorption spectra are similar to those reported for methanol solutions.²²

Absorption spectra for the remaining complexes are shown in Figure 1. Varying the solvent (isopentane, ether, acetonitrile,

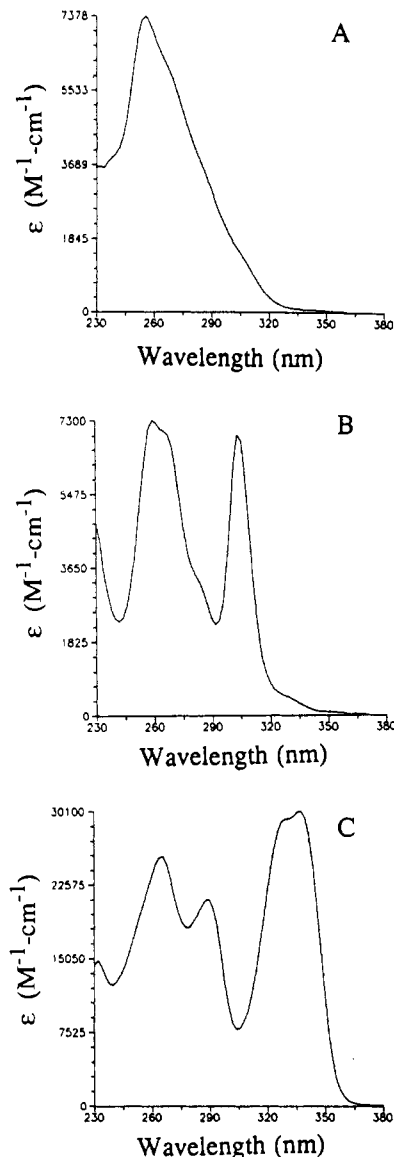


Figure 1. (A) $\text{Pt}(\text{H})\text{Cl}(\text{PEt}_3)_2$ absorption spectrum at 298 K in CH_2Cl_2 . (B) Absorption spectrum of $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$ at 298 K in CH_2Cl_2 . (C) Absorption spectrum of $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$ in CH_2Cl_2 at 298 K.

ethanol) has very little effect on the shapes or positions of the bands, although there does appear to be a very slight ($\sim 200 \text{ cm}^{-1}$) blue shift of the 304-nm band of $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$ in hydroxylic solvents. These results are in agreement with data obtained previously from bis(tertiary phosphine)dialkynylnickel(II), -palladium(II), and -platinum(II) complexes.²³ In nonpolar solvents such as isopentane and ether the 260-nm band is resolved into two maxima at 258 and 268 nm.

Emission Data. *cis*- $\text{PtCl}_2(\text{PEt}_3)_2$ and *trans*- $\text{PtCl}_2(\text{PEt}_3)_2$ were nonemissive both at room temperature and at 77 K. However, when hydride replaces one of the chlorides, the complex gives a sharp (fwhm = 830 cm^{-1}), intense, structureless emission with a maximum at $\approx 438 \text{ nm}$ at 77 K (Figure 2) and a very weak room-temperature emission.

$\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$ yields an intense structured emission in the solid state and in glass solution at 77 K (Figure 3). In the solid state, the emission is independent of wavelength. In solution at 77 K, the emission shows small but distinct spectral shifts on variation of the excitation wavelength; they do not vary monotonically with excitation wavelength. The effect is present to some degree in all glasses studied.

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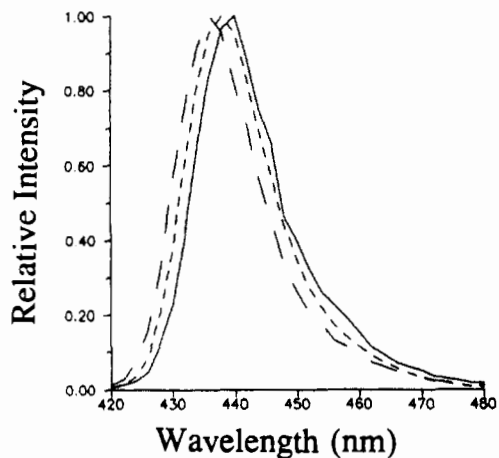


Figure 2. Emission spectra of $\text{Pt(H)Cl(PEt}_3)_2$ at 77 K in ETOMEB with excitation at 270 nm (—), 290 nm (---), and 300 nm (-.-).

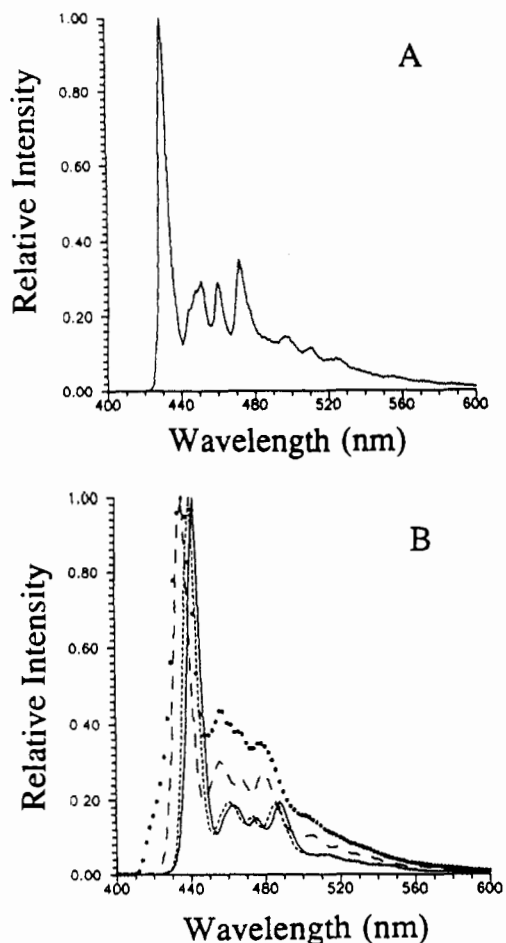


Figure 3. (A) Emission spectrum of crystalline $\text{Pt(C}\equiv\text{CPh)}_2(\text{PEt}_3)_2$ at 77 K. The spectrum was independent of excitation wavelength from 286 to 350 nm. (B) Emission spectra of $\text{Pt(C}\equiv\text{CPh)}_2(\text{PEt}_3)_2$ in ETOMEB at 77 K as a function of excitation wavelength: 328 nm (···), 332 nm (---), 342 nm (-.-), and 350 nm (—).

At room temperature, $\text{Pt(C}\equiv\text{CPh)}_2(\text{PEt}_3)_2$ emits very weakly and $\text{Pt(C}\equiv\text{CH)}_2(\text{PEt}_3)_2$ (Figure 4) emits weakly. The $\text{Pt(C}\equiv\text{CPh)}_2(\text{PEt}_3)_2$ emission appears to be structured, but is barely above the solvent background. The $\text{Pt(C}\equiv\text{CH)}_2(\text{PEt}_3)_2$ emission was independent of excitation wavelength with an average lifetime of $\approx 1.7 \mu\text{s}$.

At room temperature, all complexes show very small solvent effects on their absorption spectra. $\text{Pt(C}\equiv\text{CH)}_2(\text{PEt}_3)_2$ also shows a very small solvent effect (<2–4 nm) on its room-temperature emission spectra. At 77 K, $\text{Pt(C}\equiv\text{CH)}_2(\text{PEt}_3)_2$ shows an extraordinarily large wavelength dependence of the emission with

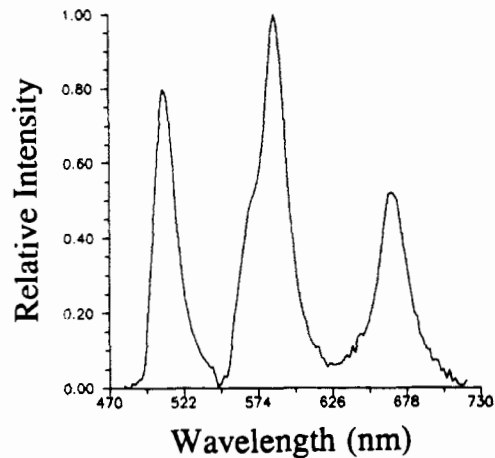


Figure 4. Emission spectrum of $\text{Pt(C}\equiv\text{CH)}_2(\text{PEt}_3)_2$ at room temperature in deaerated CH_2Cl_2 .

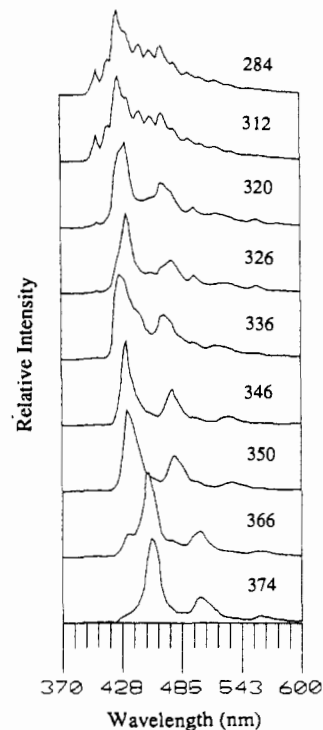


Figure 5. Emission spectra of $\text{Pt(C}\equiv\text{CH)}_2(\text{PEt}_3)_2$ at 77 K in MEB as a function of excitation wavelength. Excitation wavelengths are noted in nanometers on the vertical axis; emission wavelengths are shown in nanometers on the horizontal axis.

Table I. Luminescence Properties of Pt(II) Complexes at 77 K

compound	Φ	$\tau_0, \mu\text{s}$	$10^{-3}k_r, \text{s}^{-1}$	$10^{-4}k_{nr}, \text{s}^{-1}$	$\tau_r, \mu\text{s}$
<i>trans</i> - $\text{Pt(H)Cl(PEt}_3)_2$	0.11	38.3	2.9	2.3	350
<i>trans</i> - $\text{Pt(C}\equiv\text{CH)}_2(\text{PEt}_3)_2$	0.012	7.5 (83%)	1.3	11	778
		33.7 (17%)			
<i>trans</i> - $\text{Pt(C}\equiv\text{CPh)}_2(\text{PEt}_3)_2$	~ 1	38.2	29	0	34

excitation wavelength. Representative emission spectra are shown in Figures 5–7 for different solvents.

Table I shows the quantum yields, lifetimes, radiative and nonradiative lifetimes, and rate constants for the emissive complexes. The uncorrected excitation spectra for the three primary emission components of $\text{Pt(C}\equiv\text{CH)}_2(\text{PEt}_3)_2$ are shown in Figure 8A. Figure 8B shows the *R* values using $E(422 \text{ nm})/E(456 \text{ nm})$ and $E(434 \text{ nm})/E(456 \text{ nm})$, respectively.

Figures 9–11 show the spectral decomposition of the emission spectra for $\text{Pt(C}\equiv\text{CH)}_2(\text{PEt}_3)_2$ in several different solvents. The relative weight of each emission is indicated by the height of the

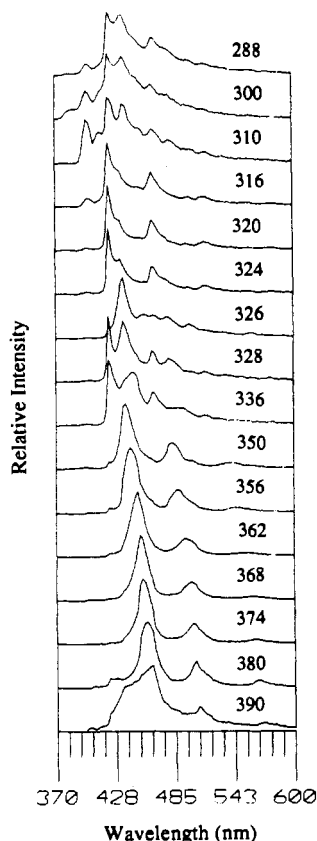


Figure 6. Emission spectra of $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$ at 77 K in ETOMEB as a function of excitation wavelength. Excitation wavelengths are noted in nanometers on the vertical axis; emission wavelengths are shown in nanometers on the horizontal axis.

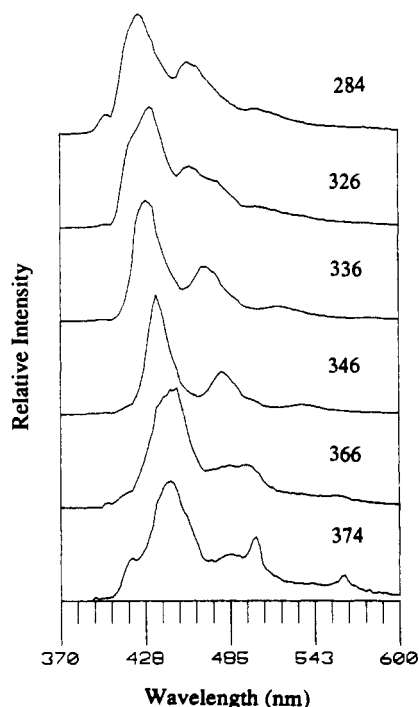


Figure 7. Emission spectra of $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$ at 77 K in MeOH/ H_2O as a function of excitation wavelength. Excitation wavelengths are noted in nanometers on the vertical axis; emission wavelengths are shown in nanometers on the horizontal axis.

vertical bar while the position of the highest energy emission band is denoted by the placement of the bar on the abscissa.

The simplest spectrum, used as the base, was generally broader than the spectra using high excitation energies. Thus, while the

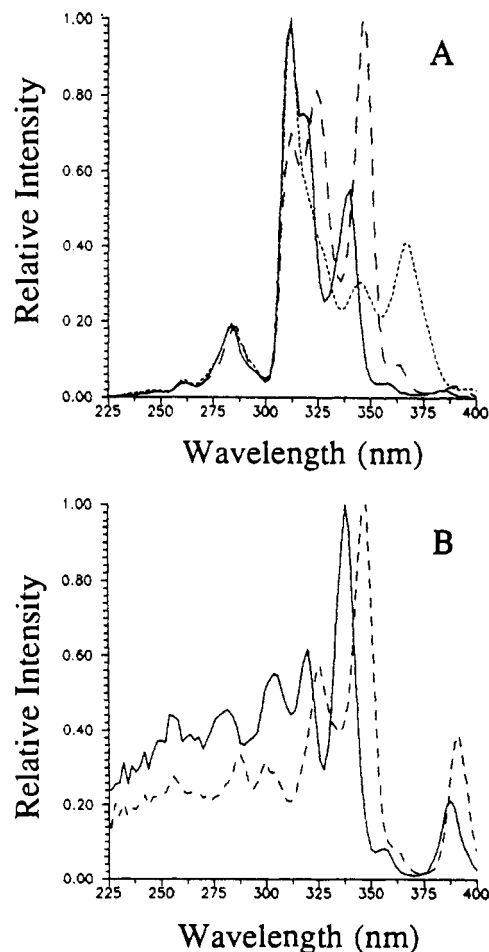


Figure 8. (A) 77 K uncorrected excitation spectra of $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$ in MEB with emission monitored at 422 (—), 434 (---), and 456 nm (-.-). (B) R plot using 422 nm/456 nm (—) and 434 nm/456 nm (-.-).

fits to the low-energy excitation spectra were excellent, the fits using the broad base-spectrum could not faithfully reproduce the narrow spectra for high-energy excitation. However, in all cases, the fits matched all spectral peaks and gave good overall fits to the complete spectra.

In light of the extreme variation in emission spectra with excitation wavelength, several procedures were performed to test for impurities and compound instability. The complexes were determined to be pure by TLC standards and were very stable. For $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$, the small amount of material available forced us to use the same sample in several different solvents. When we had finished, we remeasured the complex in the first solvent and obtained exactly the same results. Further, it is clear from our emission resolutions that there would have to be a minimum of five similarly emitting components in $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$ to reconstruct our observed emission spectra. Given the TLC purity of the complex, we discount the presence of such a large number of related species as the explanation of our complex spectra.

Discussion

Assignment of the Luminescence. Luminescence of square-planar d^8 systems is common in species such as PtCl_4^{2-} , PtLCl_2 , PtL_2 ($\text{L}=\alpha$ -diimine),²⁴ $\text{Pt}(\text{CN})_4^{2-}$,²⁵ MLX_2 , and ML_2 , where M

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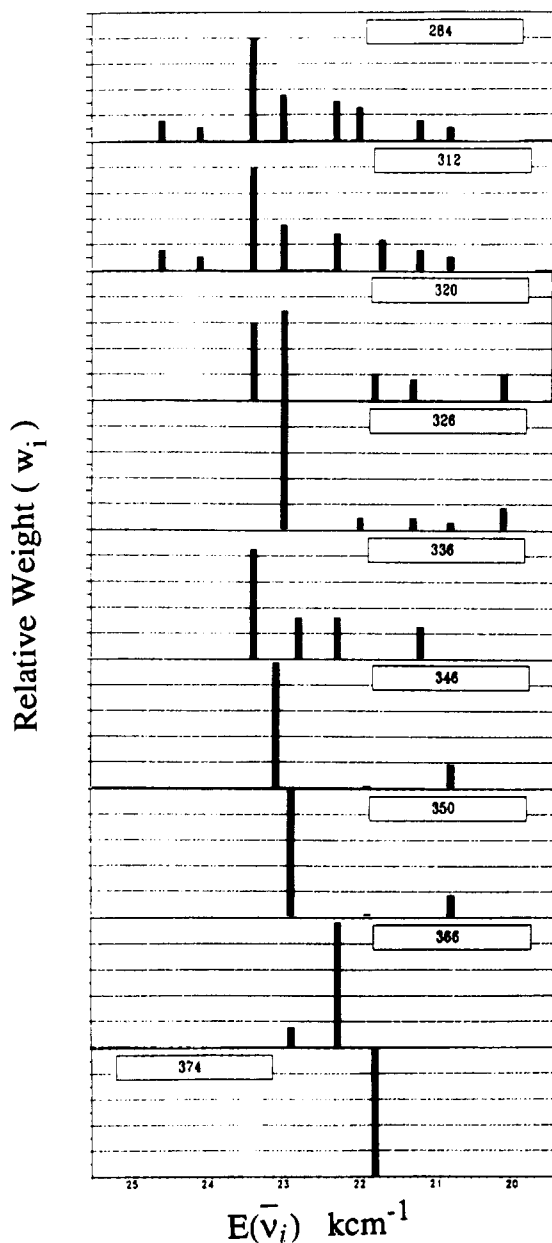


Figure 9. Decomposition of the emission spectra of $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$ at 77 K in MEB into components. The position of each bar represents the energy of a component ($E_i(\bar{\nu}_i)$) and the height represents its relative contribution (w_i) to the total spectrum.

is Pt(II), Rh(I), and Ir(I), X can be phosphines or arsines, and L can be a bidentate phosphine or arsine.²⁶ In D_{4h} microsymmetry with bonding ligands lying along the x and y axes, the lowest excited states responsible for the emissions have been attributed to states arising from electron promotions from the a_{1g} (metal d_{z^2}) orbital to the $a_{2u}(\pi)$ orbital where the $a_{2u} \pi$ orbital can arise from metal p_z and ligand p_z (π) or d orbitals. To the extent that only the metal p_z level is involved, the emissions are metal centered while greater involvement of ligand π orbitals (π_L) gives the lowest states increasing amounts of charge-transfer (CT) character. There is still considerable uncertainty about the relative contributions of metal and ligand orbitals in many of these systems. However, a comparative study of phosphorus and arsenic ligands suggest that π orbitals on P and As are not strongly involved and that, in the absence of other π systems, the lowest excited states are predominantly metal p_z in character.^{26b}

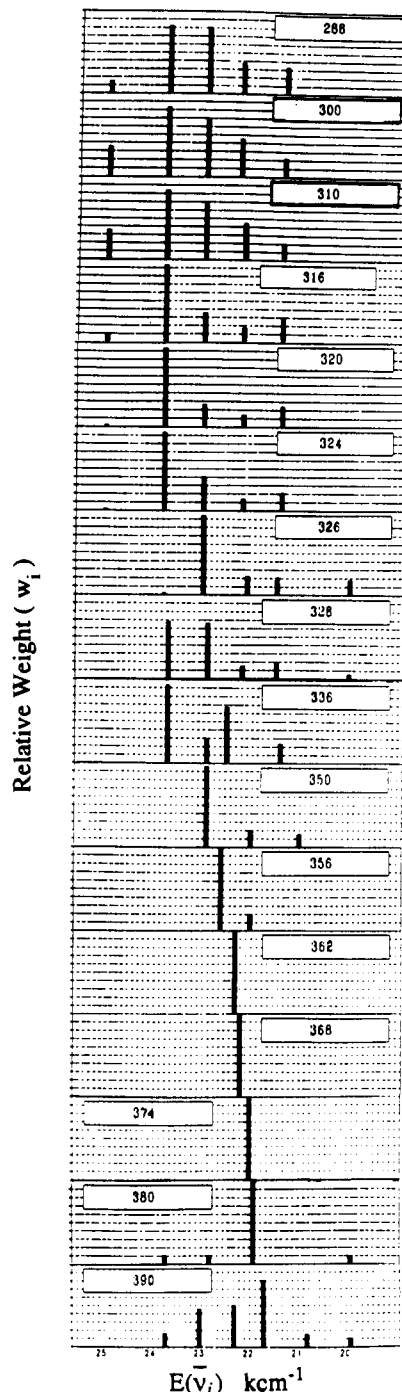


Figure 10. Decomposition of the emission spectra of $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$ at 77 K in ETOMEB into components. The position of each bar represents the energy of a component ($E_i(\bar{\nu}_i)$) and the height represents its relative contribution (w_i) to the total spectrum.

In keeping with the similar energies and structures of our emissions with those for other d^8 systems, we attribute our emissions to $a_{2u}(\pi_L:p_z) \rightarrow a_{1g}(d_{z^2})$ emissions where $\pi_L:p_z$ denotes possible orbital parentage from both the ligand π and metal p_z orbitals. We return later to the issue of the relative contributions of metal and ligand π orbitals.

We assign the emissions formally to spin-forbidden processes or phosphorescences. The radiative lifetimes are too long for fluorescences and must be phosphorescences. This is supported by the large gap between the intense spin-allowed absorptions and the emission. The long radiative lifetimes are only consistent with a spin-forbidden process. A highly structured emission is also characteristic of $a_{2u}(\pi_L:p_z) \rightarrow a_{1g}(d_{z^2})$ phosphorescences of d^8 systems. We therefore assign our emissions to $^3a_{2u}(\pi_L:p_z) \rightarrow ^1a_{1g}(d_{z^2})$ phosphorescences.

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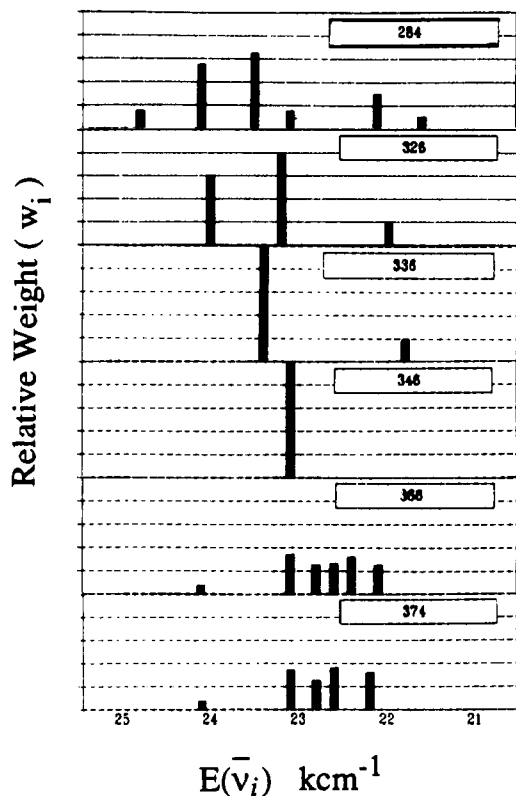


Figure 11. Decomposition of the emission spectra of $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$ at 77 K in $\text{MeOH}/\text{H}_2\text{O}$ into components. The position of each bar represents the energy of a component ($E_i(\nu_i)$) and the height represents its relative contribution (w_i) to the total spectrum.

For $\text{Pt}(\text{H})\text{Cl}(\text{PEt}_3)_2$ the emission shows virtually no high-energy vibrational structure although there is a suggestion of a very low-frequency vibration ($\approx 250 \text{ cm}^{-1}$) that might be correlated with metal–ligand vibrations. A metal hydride vibration would be at much higher energy. In the absence of any good π levels for providing low-energy ligand states, we assign the emission to a metal localized $^3a_{2u}(\text{p}_z) \rightarrow ^1a_{1g}(\text{d}_z)$ phosphorescence with very little ligand involvement.

The acetylides differ significantly from $\text{Pt}(\text{H})\text{Cl}(\text{PEt}_3)_2$. There are more intense absorption transitions toward the red relative to the hydride. Further, the more extended π system of the acetylide, the more red shifted the intense low-energy absorption bands (see Figure 1 and the much more complete compendium by Masai et al.²³). On the basis of the red shift and a weak solvent dependence of the absorptions, they have assigned these low-energy absorption bands to $^1a_{2u}(\pi_L) \leftarrow ^1a_{1g}(\text{d}_z)$. This reasonable assignment leads to a $^3a_{2u}(\pi_L) \rightarrow ^1a_{1g}(\text{d}_z)$ phosphorescence assignment for the emissions.

The structure of the emission spectra strongly supports a significant component of CT character to the emissions. Strong vibrational structure indicates that the moieties responsible for the observed vibrations are undergoing significant distortions on excitation. This fact provides a means of identifying the types of excited states involved in an emission. For example, MLCT emissions of bipyridine and phenanthroline complexes frequently exhibit strong vibrational progressions of the α -diimine ligands excited by promotion of a metal electron into a ligand π^* orbital. Similarly, metallocenes exhibiting MLCT emissions show ligand vibrational progressions.²⁷ In contrast, dd excited states of similar complexes are devoid of the α -diimine vibrations.

The single dominant vibrational progression in $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$ is clearly the $\text{C}\equiv\text{C}$ stretch. Thus, the excited state involves the π system of the ligand, which implies a significant charge-transfer component. Interestingly, the ground-state IR absorption is at 1960 cm^{-1} and differs from the emission spacing of 2100 cm^{-1} .

This discrepancy can be ascribed to the fact that the emission arises from a distorted excited-state species to a ground-state conformation of the complex, which is in a distorted geometry compared to the normal ground-state form and, thus, has a different vibrational frequency.

Similarly, the vibrations in $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$ implicate ligand excitation and, thus, an MLCT excited state. The strong vibrations on the emission of the $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$ complex correlate well with the more complex vibrations of the $\text{PhC}\equiv\text{C}$ ligand.²⁸ We observe vibrational peaks at 638 , 871 , 1102 , 1503 , 2065 , and 3176 cm^{-1} . The 638-cm^{-1} band correlates with the 639 - and 620-cm^{-1} phenyl ring skeletal vibrations, the 871-cm^{-1} band with the 871-cm^{-1} out-of-plane C–H wagging, the 1102-cm^{-1} band with the $1125/1175\text{-cm}^{-1}$ CH bends, and the 1503-cm^{-1} band with the $1488/1600\text{-cm}^{-1}$ ring C–C stretches. The 2065-cm^{-1} band is the $\text{C}\equiv\text{C}$ stretch and matches the observed 2103-cm^{-1} band seen in the IR spectrum of the complex. The 3176-cm^{-1} band may be due to either C–H stretches or combination bands. The higher energy bands are either vibrational progressions or combinations of lower energy bands.

In summary, in $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$ and $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$, the presence of strong enabling acetylide vibrations demonstrates internuclear distortion of these ligands in the excited state. The most plausible distortion mode arises from weakening of the $\text{C}\equiv\text{C}$ bond on promotion of a metal electron into the extended antibonding π^* orbital system made up from the overlapping p_z orbitals of the acetylide and the metal. This weakens the $\text{C}\equiv\text{C}$ bond and yields large equilibrium internuclear displacements to give strong excitation of these vibrations. The excitation of Ph vibrations is a clear indication of electron delocalization into the extended π system of the $\text{PhC}\equiv\text{C}$ group and further supports the claim of CT character to the excited state.

The absence of any high energy vibrational structure in $\text{Pt}(\text{H})\text{Cl}(\text{PEt}_3)_2$ arises from a lack of metal-to-ligand charge-transfer (MLCT) character even though there is a strong M–H IR band at 2183 cm^{-1} , which is not greatly different from the $\text{HC}\equiv\text{C}$ stretch. However, there is no good overlap of hydride and metal π orbitals that can give CT character to the excited state and excite the M–H vibration. The observed low-frequency vibrations would arise from weakening of the metal ligand bonds on promotion of a bonding d electron to a nonbonding p orbital.

Excitation Wavelength Effects. The exceptionally strong excitation wavelength dependence of the emissions, especially for $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$, is an unambiguous indication of a heterogeneous emission. All three complexes exhibit emission heterogeneity, although they differ greatly in the magnitude of the effects, with $\text{Pt}(\text{H})\text{Cl}(\text{PEt}_3)_2$ and $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$ having the smallest effects. It seems reasonable to assume a common origin to the effect, and we return later to the differences between the complexes. Because the effects are most pronounced with $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$, we will emphasize that complex in our discussions.

The emission heterogeneity could arise from (1) emissions from several unequilibrated states that are reached with different efficiencies with varying excitation wavelength or (2) ground-state heterogeneity of a single species.

While possible, it seems unlikely that one species could give rise to multiple emitting states that are populated with different efficiencies depending on excitation wavelength. For the existence of emission heterogeneity, the states must not be in rapid thermal equilibrium with each other. Thus, there must be at least five (see Figures 9–11), and perhaps as many as 10, nonequilibrated states spanning an energy of $\approx 2000 \text{ cm}^{-1}$. In view of the paucity of examples of even dual emissions from transition-metal complexes, the need to postulate five or more independent emissions from one molecule seems very unlikely.

We conclude that the multiple emissions arise from site heterogeneity. All of the emission spectra can be reconstructed from

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a linear combination of the simplest emission spectrum suitably shifted and scaled. This would be unlikely unless the emissions had a common electronic state origin that differed only in base energy. The relatively small number of sites observed for different excitations is not uncommon for many glass media. Also, the continuous shift in the emission energy with variation in excitation in the 320–390-nm region is a clear indication of site energy differences (vide infra) and inconsistent with a mixture.

We make no claims about the uniqueness of the fits in Figures 9–11. Other variations in relative intensity ratios could well give comparable fits. However, any good fit required at least 5–10 different spectra with different origins, and because of the sharpness of the peaks, the fits are quite sensitive to changes in these origins. We, thus, estimate that the origins are accurate to $<100\text{ cm}^{-1}$.

The assumption of identical band shapes for all the emission spectra is not completely reasonable. Emission from the same electronic state in different environments might well show small variations in bandwidths and energies. Indeed, such variations may contribute to the failure to have exact fits by using only a single base emission spectrum. However, the excellent overall agreement suggests that these differences in site spectra are not large.

Site heterogeneity is well-known and extensively studied by Shpol'skii and fluorescence line narrowing spectroscopy (FLN-S).^{27,29,30} Innumerable organics as well as chlorophylls and metallocenes have been examined. The absorption and emission lines can be extraordinarily narrow ($<1\text{ cm}^{-1}$). This is especially true for measurements made at $<20\text{ K}$ and for excitation near the 0–0 of the lowest energy excited state. Because of the spectral narrowness, it is frequently possible to see differences in the electronic origins of molecules situated in different sites. Anywhere from a few to at least seven different sites have been observed for one species. The observed range of site energies may range from a few wavenumbers to 200–400 cm^{-1} .

Since our emission bandwidths are tens to hundreds of times broader than those in lower temperature FLNS, we can see only gross shifts rather than fine detail. $\text{Pt}(\text{H})\text{Cl}(\text{PEt}_3)_2$ and $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$ show continuous shifts with excitation wavelength ($\text{Pt}(\text{H})\text{Cl}(\text{PEt}_3)_2$, $\approx 200\text{ cm}^{-1}$, and $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$, 350–600 cm^{-1} , depending on solvent matrix). These shifts are certainly in a range consistent with site heterogeneity.

For $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$ at some excitation wavelengths and $\text{Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$, the emission shifts are larger than those for FLNS. However, FLNS does not really address the existence of higher energy sites. In FLNS, there is a rapid decrease in resolution with higher energy excitations; this leads workers to study and interpret the complex, but simpler, sharp spectra arising from low-energy excitation. For an example of this decreased resolution, see the smearing out of the pyrene spectrum with increasing excitation energy.^{30a} A reasonable interpretation of this result is that higher energy excitation pumps a manifold of overlapping sites.

Additional support of a multisite heterogeneity model arises from the complete absence of emission shift with excitation wavelength for the solid $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$. If the emissions were from several nonequilibrated electronic states, we would expect that heterogeneous emission in all media including crystals, which is not observed. However, in a crystal environment, which may give only one site, the emission is completely homogeneous and much sharper than those for any of the glass spectra. Thus, the breadth and wavelength dependence on the emission for Pt-

Table II. Factors Influencing Environmental Response

complex	CT character	sample volume	steric shielding	response
$\text{trans-Pt}(\text{H})\text{Cl}(\text{PEt}_3)_2$	small	small	large	small
$\text{trans-Pt}(\text{C}\equiv\text{CH})_2(\text{PEt}_3)_2$	moderate	moderate	moderate	sensitive
$\text{trans-Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$	large	large	small	muted sensitivity

$(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2$ in glasses supports a ground-state heterogeneity effect. By analogy, this result also supports ground-state heterogeneity for the other complexes.

Given that the excitation dependencies can be attributed to site heterogeneity, we can make several observations concerning the nature of the sites. The variations in emission spectra with excitation wavelength indicates that there must be at least two general types of sites: (1) energetically widely separated sites with narrow distributions; (2) sites with broader energy distributions or a distribution of sites spanning a relatively wide energy range.

The presence of narrow distribution sites is shown by the narrow emission spectra obtained by high-energy excitation. If there were a distribution of excitable sites with a range of energies wider than the emission peaks, the emission spectra would be broadened. The wide separation of the sharp peaks shows that the accessible sites must be relatively few and narrow, as well as widely separated, in energy.

For low-energy excitation, there is not evidence for narrow emission lines except at a few wavelengths for some of the solvents. A plausible explanation for these broader features is that within a single site there is a distribution of site energies with each site component giving a narrow emission similar to that observed under higher energy excitation. The emission breadth for low-energy excitation then arises from multiple overlapping narrow emissions from these site components. Alternatively, there could be a distribution of sites with narrow emissions. The observed emission width would then arise from overlapping site emissions. We cannot differentiate between two possibilities.

Several other features of our low-temperature emission spectra are explicable within the context of the site model. The broadening of the spectra with increasing polarity is consistent with a larger number of sites for the more polar media; this distribution may approach a continuum for the most polar media. This broadening of the site distributions is seen even on high energy excitation where the spectral sharpness never approaches that for the less polar glasses.

The increasing complexity of the spectra for higher energy excitation is a consequence of increasing spectral congestion at higher energies with concomitant excitation into a larger number of sites.

The simplification of the spectra with excitation in the 320–390-nm region is a consequence of the relatively simple absorption spectrum in this region, which minimizes overlapping absorption bands and, thus, reduces overlap between energetically different sites. In addition, we were apparently fortunate at selecting excitation wavelengths that corresponded to single-site absorptions. The increasing spectral complexity with lower energy excitation in some solvents probably reflects an accidental overlapping set of different site absorption bands.

Origin of the Heterogeneity. We turn to the clues offered by these results as to the various factors governing environmental sensitivity of the emissions of our metal complexes. One could argue that some of the same factors that have been suggested as promoting exciplex formation might also enhance the impact of the local environment on the wavelength and lifetimes of various transitions. Previous work has suggested that when the electronic transition involves an electron in an "exposed" orbital, particularly if the transition has CT character, exciplex formation is favored.³¹ Since the solvent or media is occupying the same relative positions as the exciplex partner, it is reasonable to assume that this type

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of transition would also show considerable environmental sensitivity.

Table II summarizes various factors that could be expected to influence environmental sensitivity. Also shown is the contribution of each factor for our complexes as well as the observed site sensitivity (e.g. response). Within the framework of the factors of Table II, we now interpret the different behaviors of our complexes.

Since the emissions are all ${}^3a_{2u}(\pi_L:p_z) \rightarrow {}^1a_{1g}(d_{z^2})$ phosphorescences, the absence of any pronounced variations in absorption energies with solvent (solvatochromism) was surprising; the excited state involves ligand π_L and metal p_z orbitals on the open faces of the square-planar metal complexes, which should be subject to solvent perturbation. We attribute this insensitivity to two features. First, solvatochromism is most pronounced for systems exhibiting large changes in dipole moment on excitation; solvent interactions then have large opportunities of selectively affecting the ground or the excited-state energies. For example, the MLCT absorptions and emission of *cis*-Ru(bpy)₂(CN)₂ are exceptionally solvatochromic, while the MLCT transitions of Ru(bpy)₃²⁺, which has little change in dipole moment on excitation, are very small. Since the acetylides are centrosymmetric, they exhibit no change in dipole moment on excitation, and, thus, are much less prone to solvatochromic effects. Second, molecular models indicate that the Et₃P ligands are quite bulky and overlap extensively with the metal p_z region; thus, the Et₃Ps greatly shield the p_z orbitals from direct solvent perturbation. Similar alkyl chain shielding was observed for ReL(CO)₃NCR⁺ and OsL₂(CO)NCR (L = α -diimine).^{20c,32}

While Pt(H)Cl(PEt₃)₂ is not centrosymmetric, the excited state has no CT character and involves only metal d and p orbitals. Thus, the excited state is highly localized and has little change in dipole moment on excitation, and the excited portion of the complex is largely shielded from the environment by the Et₃P. These factors all contribute to making Pt(H)Cl(PEt₃)₂ a very small and insensitive antenna with very small site sensitivity and solvatochromism.

On the basis of the above considerations, we are forced to exclude conventional dipolar solvatochromism as the major source of the spectral richness of the 77 K emission spectra. We conclude that the dominant contribution is a site-specific interaction with the complexes.

In contrast to Pt(H)Cl(PEt₃)₂, Pt(C≡CH)₂(PEt₃)₂ and Pt(C≡CPh)₂(PEt₃)₂ have larger site sensitivity, but Pt(C≡CH)₂(PEt₃)₂ is much more sensitive. Both complexes have significant CT components in their excited states, and the excited volume extends beyond that shielded by the Et₃P and can, thus, feel environmental perturbations. The extended excited volume accounts for the greater site sensitivity of the acetylides versus Pt(H)Cl(PEt₃)₂.

However, since both excited states have CT character, the large differences in sensitivity of the two complexes must arise from another factor. We suggest the primary component is the excited-state volume that samples the environment. The excited state of Pt(C≡CH)₂(PEt₃)₂ is extended enough to sample the solvent shell, but small enough to crisply feel differences in local discontinuities caused by local variations in the solvent environment. In contrast, the excited volume of Pt(C≡CPh)₂(PEt₃)₂ is spatially much more extended and samples an extended solvent shell. Over such a large shell, the complex will feel an average environment and small, sharp local variations will be averaged over the entire shell. Thus, on the average, the Pt(C≡CPh)₂(PEt₃)₂ complex will show a much smaller site sensitivity.

The origin of the large site energy differences is not known at this time. However, it may involve out-of-plane bending of the complex, which enhances energy differences for different solvent configurations. Such out-of-plane distortions are not out of the question as the geometry of excited acetylene is a trans configuration.³³

We have referred to site energy differences. However, an alternative interpretation centers around the existence of different conformers or rotamers involving the Et₃P ligands. There may be several different preferential conformations that could lead to the large energy differences observed with small ligand and solvent site conformation perturbations modulating and broadening the distribution of sites. Thus, our term site may refer to the composite effect of intra-intermolecular interactions.

The large spread in site energies for the Pt(C≡CH)₂(PEt₃)₂ is not unreasonable. Although the exception rather than the rule, large energy shifts caused by relatively small environmental changes are known. The MLCT state energies of Ru(α -diimine)₃²⁺ which, to first order, have no permanent dipole moment change on excitation can be shifted by 600–1100 cm⁻¹ on going from a homogeneous to a micellar microheterogeneous environment.³⁴ Similarly, Sowinska et al.³⁵ have reported changes in emission energies of ≥ 1.2 kcm⁻¹ for the charge-transfer excited states of Ru(bpy)₂Cl(DMABN)⁺ (DMABN = (dimethylamino)benzonitrile).³⁵ They interpreted this result on the basis of nonequilibrated excited states, but an equally valid alternative interpretation is a distribution of sites with energy shifts in the Ru–DMABN MLCT state arising from site/conformer energy differences.

To summarize the effects, we expect maximum site sensitivity when the excited state samples a relatively narrow range of volumes. The excited state must not be too localized or it cannot feel differences in solvent sites, and it must not be so large as to feel an average environment that samples many solvent molecules. This latter restriction will be most stringent for polar solvents that do not pack in a very orderly fashion around the complex. Charge-transfer excited states rather than metal-localized excited states will be most likely to show site sensitivity. However, it seems likely that charged complexes or complexes with large dipole moment changes on excitation will be poorer candidates for showing a small number of discernible sites. For charged complexes, polar interactions with the charge will tend to wash out small site variations. Similarly, molecules with large dipole moment changes will show large energy variations from normal dipolar interactions that will again tend to wash out small site variations. Thus, the best candidates for showing high site sensitivity and selectivity will be relatively small, uncharged, high-symmetry complexes with charge-transfer excited states. Of course, since site energy differences tend to be small, narrow emission spectra enhance the ability to discern different sites. Narrow spectra will be most likely observed from nonpolar, uncharged complexes.

cis- and *trans*-PtCl₂(PEt₃)₂. In striking contrast to the other complexes, neither the *cis*- nor the *trans*-PtCl₂(PEt₃)₂ complex gives emissions at room temperature or 77 K. The absence of intense absorptions in the 300–400-nm region²² suggests the absence of any low-lying charge-transfer excited state. Further, the low crystal field strength of chloride versus the acetylides should lower the energy of the metal-localized dd excited states. It has been suggested that the lowest excited state in these complexes is a dd state, and the excited state is tetrahedral rather than square planar. This claim is supported by the facile *cis*–*trans* photoisomerization.²² This excited-state geometric distortion lowers the excited energy relative to the ground state and enables very fast radiationless deactivation to the ground state. This mechanism has been evoked for the absence of luminescence of other square-planar Pt complexes with relatively weak field ligands.

Conclusions

Remarkably narrow emission spectra for several Pt(II) complexes coupled with site-selective spectroscopy has been observed.

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Depending on excitation wavelength, the spectra can be very simple or quite complex. However, in all cases, a relatively small number of sites, some probably with distributions of their own, can be used to fit all observed spectra. This indicates that remarkably few sites are present or that the spectra of the different sites are narrow enough to permit selective excitation of a relatively small number of sites at any one time.

The wide differences in emission behavior of our complexes are explained on the basis of several criteria. We suggest that criteria can be used to fabricate systems that can show enhanced microscopic site selectivity.

The relatively small number of sites coupled with the narrowness

of the 77 K spectra suggests that these systems are candidates for Shpol'skii spectra or fluorescence line narrowing. Particularly promising are spectra measured from hydrocarbon glasses at lower temperatures than we can currently reach.

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Excited-State Annihilation Process Involving a Cyclometalated Platinum(II) Complex

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The Pt(tpy)(ppz) complex exhibits strong luminescence with a relatively long excited-state lifetime (15.3 μ s) in deaerated acetonitrile solution, at room temperature and at low excitation intensity, and can be easily involved in excited-state quenching processes. The ³CT excited state is, in fact, quenched (i) by oxygen ($k_q \approx 10^9$ M⁻¹ s⁻¹), (ii) by the ground-state complex ($k_q = 5.7 \times 10^7$ M⁻¹ s⁻¹), and (iii) by another ³CT excited state in an annihilation process, which is practically diffusion controlled ($k_3 > 6 \times 10^9$ M⁻¹ s⁻¹). The ground-state quenching and the annihilation process most probably occur via an excimer formation mechanism.

Introduction

The search for a transition-metal compound with suitable photochemical, photophysical, and redox properties to be used as photosensitizer in energy- and/or electron-transfer processes,²⁻⁸ has been mainly performed within the Ru(II) polypyridine family.^{5,9,10} Recently, an increasing interest in cyclometalated complexes has emerged. These compounds, which contain ligands that are structurally similar to polypyridines, have long been recognized in the literature,^{8,11} but their photophysical characterization has only been reported in the last few years.¹²⁻¹⁸

We have already reported the photochemical and photophysical properties of cyclometalated Rh(III),¹⁹⁻²¹ Pt(II),^{13,21-24} Pd(I-

I),^{21,23,25} and Pt(IV)^{21,26} complexes.

Continuing our investigation in this field, we report here a cyclometalated Pt(II) complex (Figure 1), whose unusual excited-state behavior can be accounted for by an excited-state annihilation process.

This process is well-known for organic molecules,²⁷ but only few examples have been reported in the literature in the field of coordination compounds.²⁸⁻³⁰

Experimental Section

The preparation of Pt(tpy)(ppz) has been reported previously.²⁴ Polarographic grade acetonitrile (AN) was always used.

When necessary, the solutions were degassed by repeated freeze-pump-thaw cycles.

The absorption spectra were recorded with a Kontron Uvikon 860 spectrophotometer. Emission spectra (uncorrected) and emission quantum yields were obtained with a Perkin-Elmer LS5 spectrofluorimeter equipped with a Hamamatsu R928 phototube. Emission quantum yields were referred to an aerated Ru(bpy)₃²⁺ aqueous solution.^{31,32}

Emission lifetimes were measured with either a single-photon-counting apparatus (Edinburgh Instruments, Model 199) or a laser flash photolysis apparatus having as excitation source a JK system 2000 neodymium YAG DLPY4 laser ($\lambda_{exc} = 355$ nm, pulse half-width = 25 ns, pulse

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