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Lowest Electronic Excited States of Platinum(II) Diimine Complexes

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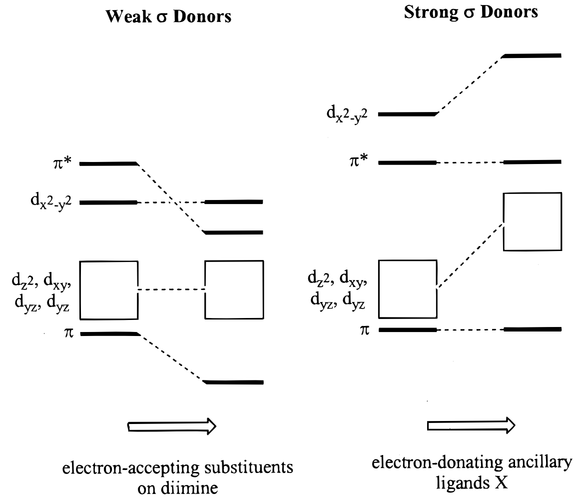
Absorption and emission spectra of Pt(diimine)L_2 complexes (diimine = 2,2′-bipyridine (bpy) or 4,4′-dimethyl-2,2′-bipyridine (dmbpy); L = pyrazolate (pz^-), 3,5-dimethylpyrazolate ($dmpz^-$), or 3,4,5-trimethylpyrazolate ($tmpz^-$)) have been measured. Solvent-sensitive absorption bands (370−440 nm) are attributed to spin-allowed metal-to-ligand charge-transfer (^{1}MLCT) transitions. As solids and in 77 K glassy solution, Pt(bpy)$(pz)_2$ and Pt(dmbpy)$(pz)_2$ exhibit highly structured emission systems ($\lambda_{max} \approx$ 494 nm) similar to those of the diprotonated forms of these complexes. The highly structured bands (spacings 1000−1400 cm^{-1}) indicate that the transition originates in a diimine-centered $^3(\pi \rightarrow \pi^*)$ (^{3}LL) excited state. The intense solid-state and 77 K glassy solution emissions from ^{3}MLCT[d(Pt)→π^*(bpy)] excited states of complexes with $dmpz^-$ and $tmpz^-$ ligands occur at longer wavelengths (λ_{max} = 500−610 nm), with much broader vibronic structure. These findings are consistent with increasing electron donation of the pyrazolate ligands, leading to a distinct crossover from a lowest ^{3}LL to a ^{3}MLCT excited state.

Introduction

Emission has been observed from both triplet ligand field (^{3}LF) and intraligand $^3(\pi \rightarrow \pi^*)$ (^{3}LL) excited states of platinum(II) diimine monomers.[1−4] The energetic order of these states depends on the nature of the ancillary ligands: the broad red emission of Pt(bpy)X_2 (X = Cl, Br, I; bpy = 2,2′-bipyridine) originates from a ^{3}LF excited state (Pt(bpy)Cl_2: λ_{max} = 641 nm; full width at half-maximum (fwhm) = 4000 cm^{-1}; τ = 500 ns at 250 K);[4] Pt(bpy)(en)$^{2+}$ (en = ethylenediamine), however, exhibits sharply structured green emission attributable to a transition from a diimine-centered ^{3}LL excited state ([Pt(bpy)(en)]$(ClO_4)_2$: λ_{max} = 461, 482sh, 492, 521, 530sh, 569sh, 607sh nm; τ = 1400 ns at 300 K).[1]

A spin-allowed metal-to-ligand charge-transfer (^{1}MLCT) [d(Pt)→π^*(diimine)] transition is often observed to lower energy of the ^{1}LL bands in the absorption spectra of platinum(II) diimine complexes.[1,2,4,5] This finding suggests two possible strategies for tuning the electronic structures of these complexes (Scheme 1). These strategies are distinguished by whether the ancillary ligands X are strong or weak σ donors. For weak σ donors, illustrated by Pt(3,3′-$(CO_2Me)_2$bpy)Cl_2, substitution of electron-withdrawing groups on the diimine stabilizes the ligand π^* level relative to the antibonding $d_{x^2-y^2}$(Pt) level.[4] Since the diimine π levels are also stabilized, the lowest ^{3}MLCT excited state lies at lower energy than the lowest ^{3}LF and ^{3}LL states, and an asymmetric orange emission is observed (λ_{max} = 556sh, 587, 667sh nm; fwhm = 2900 cm^{-1}; τ = 350 ns at 300 K). In the case of ancillary ligands that are strong σ donors, the empty Pt $d_{x^2-y^2}$ level is located well above the diimine π^* level. It was suggested[4] that strongly electron-donating ancillary ligands (*e.g.*, X = alkyl or aryl)[6] would effectively destabilize the filled platinum d levels relative to the diimine π and π^* levels, and therefore place a ^{3}MLCT excited state below the ^{3}LL state (Scheme 1). The bipyridylbis(pyrazolyl)platinum(II) complexes reported here fall into this second category; they exhibit emission from either a ^{3}LL or ^{3}MLCT excited state, depending on the donor properties of the ancillary pyrazolate ligands.

Scheme 1



Experimental Section

All reagents were obtained from Aldrich and used without further purification, unless specified. Tetrahydrofuran (THF) was distilled under argon from sodium and benzophenone prior to use, and dichloromethane

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was distilled under argon from CaH$_2$. Spectroscopic grade methanol was supplied by Burdick and Jackson. Solution emission samples were typically freeze/pump/thaw cycled four times to give a final pressure of less than 10^{-3} mTorr. Room-temperature solution samples were contained in a 1 cm path length quartz cuvette; 77 K glassy solutions were prepared by inserting a quartz EPR tube containing the solution into a quartz-tipped finger dewar. Solid-state samples were contained in a quartz EPR tube or a sealed quartz capillary tube; for low-temperature measurements, the sealed capillary tube was placed in a CTI 350CP closed-cycle He refrigerator from Janis Research. Elemental analyses were carried out by Galbraith Laboratories, Inc., or by F. Harvey of Caltech. Mass spectra were obtained from the Caltech Mass Spectrometry Laboratory.

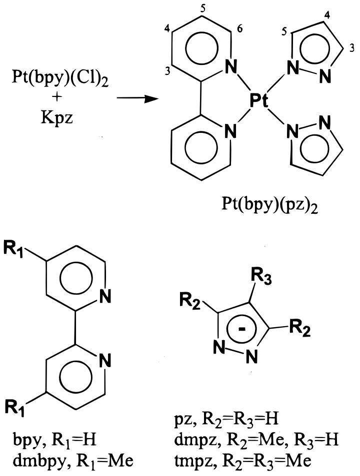
Instrumentation. ^{1}H NMR spectra were obtained using a Bruker AM500 spectrometer. UV−vis spectra were recorded using a Cary-14 spectrometer upgraded by OLIS to include computer control.

Emission spectra of solid samples[7,8] and glassy solutions[1,4] were corrected for instrumental response. Since the platinum(II) pyrazolate complexes are only weakly luminescent in room-temperature fluid solution, emission data were obtained using the 441.6 nm line (∼20 mW) from a He/Cd laser as an excitation source. The emission was collected at 90° and dispersed using a Spex 1403 0.85 m double spectrometer equipped with a cooled R955 Hamamatsu PMT and an ORTEC 9315 single-photon counter. Room-temperature solution luminescence spectra were not corrected for instrumental response.

Excitation pulses for solution emission lifetimes[9] were generated using a Quanta-Ray Nd:YAG laser (third harmonic: 355 nm) or a Lambda Physik LPX210i XeCl excimer-pumped Lambda Physik FL3002 dye laser (PBBO, 396 nm). The emission was passed through a monochromator prior to detection using a R955 Hamamatsu PMT. Data were analyzed using least-squares fitting programs (KINFIT and DECON) written by J. R. Winkler (Caltech). For solid-state emission lifetimes,[1] the sample was excited using the third harmonic (355 nm) of a Quanta-Ray DCR3 Nd:YAG laser. The beam was severely attenuated to avoid sample heating and artifacts; measurements were made with different excitation intensities to ensure that the emission intensity was linear with excitation intensity. The emitted light was passed through Schott KV nonfluorescing cutoff filters and detected using a R928 PMT.

Synthesis. Pt(bpy)Cl$_2$ and Pt(dmbpy)Cl$_2$ (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) were prepared as described by Morgan and Burstall[10] and by Bielli and co-workers.[11] Potassium pyrazolate salts were obtained by reacting the pyrazole acid with potassium metal in dry THF. Pt(bpy)(pz)$_2$ and its derivatives were synthesized using a modification of the literature preparation.[12] For example, 0.80 g of K(dmpz) and 0.95 g of Pt(dmbpy)Cl$_2$ were refluxed in approximately 20 mL of THF for 5 h under argon. The filtered yellow solid was washed with ether. The crude product was more brightly colored if the Pt(diimine)Cl$_2$ starting material was recrystallized from *N*,*N*-dimethylformamide (DMF). Typically, the crude product was recrystallized first from dichloromethane, and then from methanol. Analysis of the solid products indicates a tendency to retain a water of crystallization. Solid samples used in spectroscopic studies were rigorously dried and contained 0.5 or fewer water molecules per platinum complex with the exception of Pt(dmbpy)(tmpz)$_2$·H$_2$O. Anal. Found (Calcd): Pt(bpy)(pz)$_2$·0.5H$_2$O, C, 38.68 (38.87); H, 2.99 (3.06); N, 17.25 (17.0); O, 1.25 (1.62); Pt(bpy)(dmpz)$_2$, C, 43.62 (44.36); H, 3.86 (4.09); N, 15.27 (15.52); O, <0.5 (0.0); Pt(bpy)(tmpz)$_2$·0.5H$_2$O, C, 45.26 (45.67); H, 4.65 (4.70); N, 14.46 (14.52); O, 1.20 (1.38); Pt(dmbpy)(pz)$_2$, C, 41.69 (42.11); H, 3.48 (3.53); N, 16.02 (16.37); O, 0.53 (0.0); Pt(dmbpy)(dmpz)$_2$·0.5H$_2$O, C, 45.39 (45.67); H, 4.33 (4.70); N, 14.34 (14.52); O, 0.61 (1.38); Pt(dmbpy)(tmpz)$_2$·H$_2$O, C, 46.12 (46.82); H, 4.78 (5.24); N, 13.43 (13.65); O, 2.25 (2.60). FAB-MS (*m*/*z*): 486.1 [Pt(bpy)(pz)$_2^+$], 542.1 [Pt(bpy)(dmpz)$_2^+$], 570.1 [Pt(bpy)(tmpz)$_2^+$], 514.1 [Pt(dmbpy)(pz)$_2^+$], 570.1 [Pt(dmbpy)(dmpz)$_2^+$], 598.2 [Pt(dmbpy)(tmpz)$_2^+$]. ^{1}H NMR (methanol-d_4): δ (Pt(bpy)(pz)$_2$) 6.11 (dd, 2H), 7.16 (d, 2H), 7.55 (dd, 2H), 7.57 (d, 2H), 8.10 (d, 2H), 8.25 (dd, 2H), 8.40 (d, 2H); (Pt(bpy)(dmpz)$_2$) 1.80 (s, 6H), 2.20 (s, 6H), 5.63 (s, 2H), 7.54 (dd, 2H), 8.05 (d, 2H), 8.22 (dd, 2H), 8.36 (d, 2H); (Pt(bpy)(tmpz)$_2$) 1.79 (s, 6H), 1.81 (s, 6H), 2.15 (s, 6H), 7.53 (dd, 2H), 8.00 (d, 2H), 8.22 (dd, 2H), 8.35 (d, 2H); (Pt(dmbpy)(pz)$_2$) 2.46 (s, 6H), 6.09 (dd, 2H), 7.14 (d, 2H), 7.35 (d, 2H), 7.54 (d, 2H), 7.87 (d, 2H), 8.25 (s, 2H); (Pt(dmbpy)(dmpz)$_2$) 1.79 (s, 6H), 2.18 (s, 6H), 2.45 (s, 6H), 5.61 (s, 6H), 7.34 (d, 2H), 7.84 (d, 2H), 8.21 (s, 2H); (Pt(dmbpy)(tmpz)$_2$) 1.80 (s, 6H), 1.81 (s, 6H), 2.13 (s, 6H), 2.44 (s, 6H), 7.34 (dd, 2H), 7.81 (d, 2H), 8.22 (d, 2H).

Scheme 2



Results and Discussion

Preparation and Characterization. Six bipyridylbis(pyrazolyl)platinum(II) complexes were prepared by reaction of the appropriate Pt(diimine)Cl$_2$ complex and potassium pyrazolate salt.[12] These compounds correspond to permutations of diimine ligands, bpy and dmbpy, with the deprotonated pyrazole acid derivatives, pyrazolate (pz$^-$), 3,5-dimethylpyrazolate (dmpz$^-$), and 3,4,5-trimethylpyrazolate (tmpz$^-$) (Scheme 2). On occasion, we will refer to the various substituted pyrazolate ligands as a group, in which case we use the notation pz*. The compounds form yellow to red-orange air-stable solids. The colors of the complexes with dmpz$^-$ and tmpz$^-$ ligands depend on whether the samples are wet or dry. As noted by others,[12] Pt(bpy)(dmpz)$_2$ is yellow when wet with solvent, but orange when dry. (The wet and dry forms exhibit orange emission at room temperature, and have identical ^{1}H NMR and UV−vis spectra in methanol solution.) Several other platinum(II) complexes are known to exhibit similar vapochromic behavior.[11,13−16] Analyses of samples that were dried for days at >80 °C under vacuum indicate the presence of fewer than 0.5 water molecule per platinum complex. The crystal structure of Pt(dmbpy)(pz)$_2$·H$_2$O·0.5THF[17] reveals a chain of metal complexes and water molecules connected by hydrogen bonds from the pyrazolate

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Table 1. UV−vis Spectroscopic Data (λ, nm) for Bipyridylbis(pyrazolato)platinum(II) Complexes in Methanol [ϵ, M^{-1} cm^{-1}]

compound	$^1(\pi\rightarrow\pi_2{}^*)$	$^1(\pi\rightarrow\pi_1{}^*)$	^{1}MLCT	^{3}MLCT
$Pt(bpy)(pz)_2$	248 [18 650]	309, 321 [9300, 10 400]	369 [2400]	420(sh) [780]
$Pt(bpy)(dmpz)_2$	245 [21 800]	296(sh), 308, 319 [9420, 10 350, 9390]	379 [2560]	440(sh) [670]
$Pt(bpy)(tmpz)_2$	240 [26 790]	297(sh), 307, 318 [10 000, 11 200, 10 130]	386 [2400]	460(sh) [710]
$Pt(dmbpy)(pz)_2$	248 [21 720]	294(sh), 307, 319 [8740, 9630, 11 470]	361 [2980]	410(sh) [1100]
$Pt(dmbpy)(dmpz)_2$	245 [23 620]	295(sh), 304, 317 [10 200, 10 550, 9301]	372 [2910]	430(sh) [750]
$Pt(dmbpy)(tmpz)_2$	240 [28 440]	305, 317 [10 830, 10 120]	374 [2340]	440(sh) [710]

Table 2. UV−vis Spectroscopic Data (λ, nm) for Bipyridylbis(pyrazolato)platinum(II) Complexes in Dichloromethane [ϵ, M^{-1} cm^{-1}]

compound	$^1(\pi\rightarrow\pi_2{}^*)$	$^1(\pi\rightarrow\pi_1{}^*)$	^{1}MLCT	^{3}MLCT
$Pt(bpy)(pz)_2$	249 [17 130]	322(sh) [6890]	363(sh), 393, 415(sh) [2100, 2820, 2410]	455(sh) [880]
$Pt(bpy)(dmpz)_2$	251 [22 950]	304, 318(sh) [11 700, 9300]	402 [2430]	480(sh) [690]
$Pt(bpy)(tmpz)_2$	251 [21 780]	305, 318(sh) [11 500, 9450]	412, 440(sh) [1810, 1600]	510(sh) [580]
$Pt(dmbpy)(pz)_2$	251 [20 540]	319 [7220]	357, 365(sh), 381 [2600, 2600, 2700]	430(sh) [1370]
$Pt(dmbpy)(dmpz)_2$	248, 253 [23 250, 23 120]	303(sh), 315(sh) [11 290, 8450]	391 [2480]	470(sh) [600]
$Pt(dmbpy)(tmpz)_2$	248 [24 400]	302, 315(sh) [11 700, 9710]	392, 435(sh) [2040, 1480]	490(sh) [570]

noncoordinating nitrogen to a bridging water; thus, the tenacity with which these complexes retain water is attributable to the basicity of the pyrazolate ligands. In a study of $Ru(bpy)_2(pz)_2\cdot H_2O$, it was found that the water of crystallization in this material is tightly held and no anhydrous solid form could be isolated; the pK_a of the conjugate acid ($(Ru(bpy)_2(pz)(pzH)^+)$) was estimated to be >13.[18]

The ^{1}H NMR spectrum of $Pt(bpy)(pz)_2$ is in agreement with that reported previously,[12] and the spectra of the remaining compounds have been assigned accordingly. Methyl substitution at the 4 and 4′ positions of the bipyridyl ligand results in a modest upfield shift (0.1−0.2 ppm) of the bipyridyl proton resonances, and only slightly affects the chemical shift of the pyrazolate resonances. Substitution of the pyrazolate ligands causes a small upfield shift of the bipyridyl resonances (0.1 ppm); the 6-H position is the most affected, most likely because of a through-space interaction. We conclude from these results that methyl substitution of the pyrazolate ligand increases the electron density on the platinum.

Absorption Spectroscopy. The UV−vis absorption data for these compounds are summarized in Tables 1 and 2. Spectra for $Pt(bpy)(pz)_2$ and $Pt(bpy)(dmpz)_2$ are shown in Figures 1 and 2. In these spectra, characteristic vibronic structure of the diimine-centered LL transition, $^1(\pi\rightarrow\pi_1{}^*)$, lies near 300−320 nm. However, in methylene chloride these features are not well-resolved as a result of overlapping charge-transfer transitions. A second solvent-insensitive band occurs near 250 nm in the spectrum of each complex. This band is assigned to a higher-energy spin-allowed LL transition, $\pi\rightarrow\pi_2{}^*$, centered on the bipyridyl ligand. Analogous bands are observed in the spectra of $Pt(bpy)Cl_2$[5] and $Ir(bpy)_3{}^{2+}$.[19]

At longer wavelengths (360−510 nm), there are two bands that undergo a distinct bathochromic shift with decreasing solvent polarity. The lower-energy band (410−510 nm) is considerably weaker and occurs as a shoulder on the higher-energy band (360−420 nm). In the case of $Pt(bpy)(pz)_2$, the maximum of the higher-energy feature shifts by 940 cm^{-1} from 379 nm in acetonitrile to 393 nm in dichloromethane (and to 399 nm in THF, Figure 2a); the ^{1}MLCT transition of $Pt(bpy)Cl_2$ undergoes a comparable shift (800 cm^{-1}). The two bands also shift to lower energy with increasing methyl substitution of the pyrazolate ligands (CH_2Cl_2 solution: $dmpz^-$, 402 and 480(sh) nm; $tmpz^-$, 412 and 510(sh) nm). However, methyl substituents on the bipyridyl ligand induce a slight blue shift (CH_2Cl_2: bpy, 393 and 455(sh) nm; dmbpy, 381 and 430(sh) nm). This behavior is consistent with either MLCT or LMCT transitions. However, since $Pt(pz)_2(pzH)_2$[20] and $Pt(dmpz)_2(dmpzH)_2$ are colorless and have no similar low-lying transitions,[21] the possibility of low-lying pyrazolate-localized or pyrazolate/Pt charge-transfer transitions is eliminated. By anal-

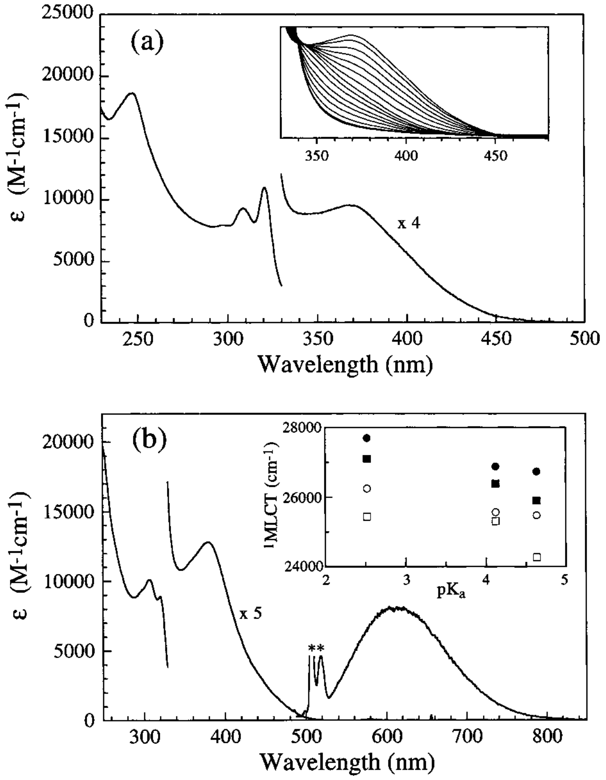

Figure 1. (a) Room-temperature absorption spectra of $Pt(bpy)(pz)_2$ in methanol solution. The inset shows the changes in the absorption spectrum of $Pt(bpy)(pz)_2$ upon titration with 2 equiv of HNO_3. An isosbestic point is observed at 345 nm during addition of the first equivalent, and at 341 nm during the addition of the second equivalent. (b) Absorption and uncorrected emission spectra of $Pt(bpy)(dmpz)_2$ in methanol solution. Strong solvent Raman lines in the emission spectrum are marked by an asterisk. The inset in (b) shows the ^{1}MLCT absorption band maximum for the six $Pt^{II}(diimine)(pz^*)_2$ complexes plotted as a function of the pK_a of the free pyrazole acid: □, $Pt(bpy)(pz^*)_2$; ○, $Pt(dmbpy)(pz^*)_2$ in CH_3OH; ■, $Pt(bpy)(pz^*)_2$; ●, $Pt(bpy)(pz^*)_2$ in CH_2Cl_2.

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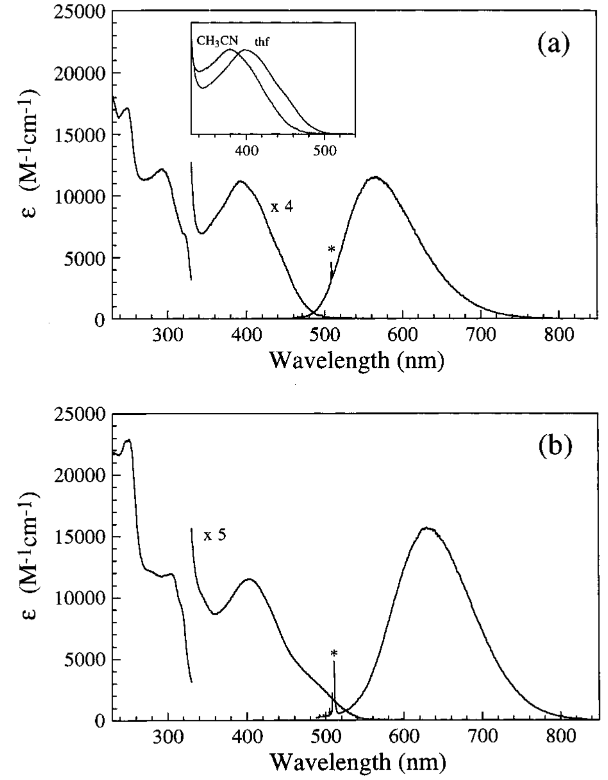

Figure 2. Room-temperature absorption and uncorrected emission spectra of (a) Pt(bpy)(pz)$_2$ and (b) Pt(bpy)(dmpz)$_2$ in dichloromethane solution. Strong solvent Raman lines are marked by an asterisk; weaker lines appear between 460 and 510 nm. The inset in (a) shows the absorption spectrum of Pt(bpy)(pz)$_2$ in CH$_3$CN and THF.

ogy to literature assignments for related Pt(diimine)X$_2$ (X = Cl, Br, I) systems,[1,4,5] we assign the higher-energy band to ^{1}MLCT[d(Pt)$\rightarrow\pi^*$(bpy)] excitation and the shoulder at lower energy to a transition to the corresponding triplet state. From the band intensity of the spin-forbidden transition, which is ~30% of that of the singlet−singlet band, it is evident that the triplets and singlets are heavily mixed *via* spin−orbit coupling. A weak shoulder appears ~2000 cm^{-1} to the blue of the ^{1}MLCT absorption band for Pt(bpy)(pz)$_2$ in dichloromethane solution (Figure 2a), and similar structure is observed in the absorption spectra of the other complexes, as well as in the 77 K excitation spectra (Figures 3 and 4). Though the C_{2v}-symmetric Pt(diimine)L$_2$ system is predicted to have four symmetry-allowed ^{1}MLCT transitions (Scheme 3), from overlap considerations only the $d_{xz+yz} \rightarrow \pi^*$(bpy) transition involving strong d/π^* interaction is predicted to be intense.[22] Therefore, it seems reasonable to assign these features to vibronic components of the MLCT[$d_{xz,yz} \rightarrow \pi^*$(bpy)] transition.

The apparent singlet−triplet splittings of the MLCT states vary somewhat erratically in the range 3000−5000 cm^{-1} (Table 2), but this is largely attributable to the poor spectroscopic resolution of the shoulder assigned to the singlet−triplet transition. Nevertheless, the splittings are considerably smaller than the bipyridyl LL singlet−triplet gap estimated from the absorption spectra of Pt(bpy)Cl$_2$ (9500 cm^{-1})[23] and Pt(bpy)(en)$^{2+}$ (9300 cm^{-1}).[1] Since the singlet−triplet splitting is given by twice the magnitude of the exchange integral, this gap increases with decreasing spatial separation of the unpaired electrons in the excited state. Whereas the LL singlet−triplet

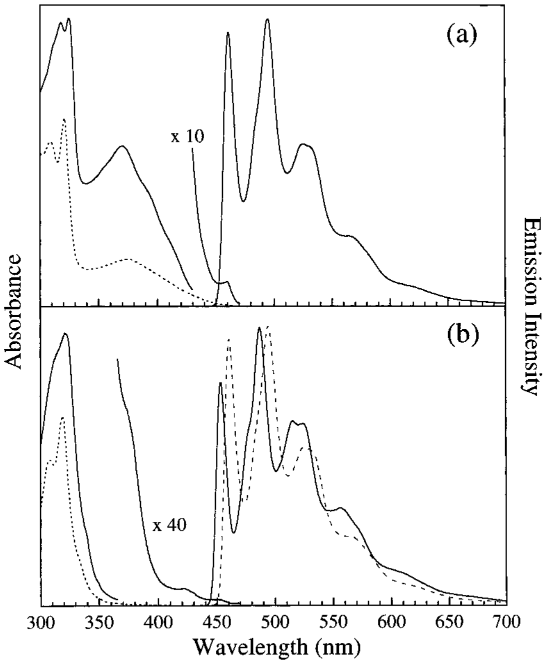

Figure 3. Ethanol−methanol (3:1) (77 K) frozen glass emission and excitation spectra of 40 μM Pt(bpy)(pz)$_2$ with (a) 1000 equiv of NEt$_3$ (λ_{ex} = 366 nm, λ_{obs} = 495 nm) (—) and (b) 100 equiv of CF$_3$COOH (λ_{ex} = 310 nm, λ_{obs} = 487 nm) (—). Room-temperature absorption spectra (···) are also shown. The emission spectrum in (a) is duplicated in (b) (- - -) to facilitate visual comparison.

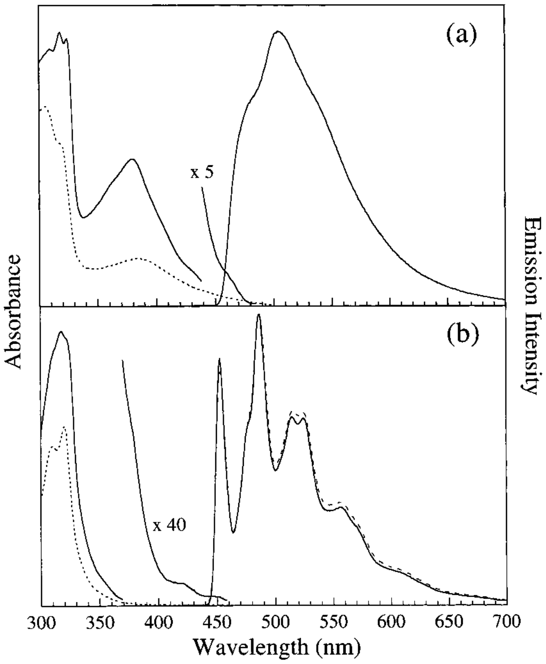

Figure 4. Ethanol−methanol (3:1) (77 K) frozen glass emission and excitation spectra of 40 μM Pt(bpy)(dmpz)$_2$ with (a) 2000 equiv of NEt$_3$ (λ_{ex} = 366 nm, λ_{obs} = 504 nm) and (b) 2000 equiv of CF$_3$COOH (λ_{ex} = 310 nm, λ_{obs} = 487 nm). The room-temperature absorption spectrum (···) is also shown to facilitate visual comparison. The 77 K ethanol−methanol emission spectrum of Pt(bpy)(pz)$_2$ with 100 equiv of CF$_3$COOH (λ_{ex} = 310 nm) from Figure 3b is shown in (b) (- - -).

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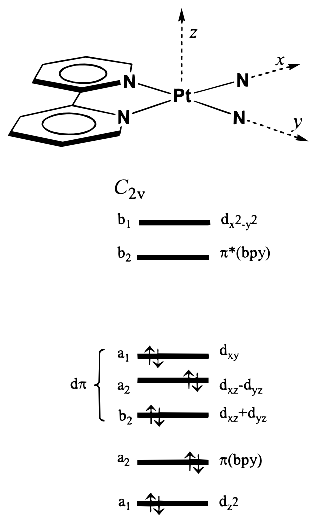
[22] The symmetry-adapted combinations $(1/\sqrt{2})(d_{xz} + d_{yz})$ and $(1/\sqrt{2})(d_{xz} - d_{yz})$ have b$_2$ and a$_2$ symmetries, respectively. The former is involved in a bonding interaction with the diimine π^*(b$_2$) LUMO, and therefore may be expected to give rise to an intense MLCT transition. It should be noted, however, that the latter combination can interact strongly with the filled diimine π(a$_2$) level, and the corresponding MLCT transition also could carry significant intensity.

[23] Connick, W. B.; Miskowski, V. M.; Houlding, V. H.; Gray, H. B. manuscript in preparation.

Scheme 3



gap is comparable to the splitting of LL states in aromatic molecules such as anthracene (11 580 cm^{-1}),[24] the MLCT singlet−triplet splitting is consistent with an excited state in which there is charge separation. For comparison, the MLCT-[$d\pi \rightarrow \pi^*$(bpy)] singlet−triplet gap is ∼3500 cm^{-1} for Pt(3,3′-$(CO_2Me)_2$bpy)Cl_2)[4] and ∼2000 cm^{-1} for $Ru(bpy)_3^{2+}$.[25]

The 400−800 cm^{-1} blue shift in the MLCT bands arising from methyl substitution of the bipyridyl ligand is attributable to destabilization of the π^* level by electron-donating methyl substituents (σ inductive effect). In accord with this model, the diimine-centered reduction potential of $Ru(dmbpy)_3^{2+}$ is cathodically shifted by 110 mV (∼900 cm^{-1}) relative to that of $Ru(bpy)_3^{2+}$.[26] The red shift of the MLCT bands with increasing methyl substitution of the pyrazolate ligands is consistent with increasing electron donation to the metal by the anionic ancillary ligands. The ancillary ligands are expected to influence the energy of MLCT states primarily by perturbing the metal d levels, and electron-donating groups will destabilize these levels. In fact, the observed red shift parallels the relative pK_a values of pzH (2.52), dmpzH (4.12), and tmpzH (4.63) (Figure 1b).[27] Conversely, electron-withdrawing groups on the pyrazolate ligands are expected to destabilize MLCT states. Thus, titration of a yellow methanol solution of Pt(bpy)$(pz)_2$ with 2 equiv of HNO_3 causes the solution to turn colorless as protonation of the pyrazolate ligands induces a dramatic blue shift of MLCT absorptions ($\lambda_{max} < 330$ nm) (Figure 1a).

Photoelectron spectra of pzH and dmpzH show that methyl substitution strongly destabilizes the nitrogen lone pair (ΔIP = 0.55 eV) and ring π orbitals (ΔIP = 0.63, 0.75 eV), suggesting that coordination of the methylated pyrazolyl ligand will destabilize metal d levels through increased σ and π donation.[28] In support of this notion, electronic structural studies of pyrazolyl-bridged Ir(I) dimers indicate that σ and π inductive effects are responsible for destabilization of the filled metal d orbitals ($d\pi$, d_{z^2}) of $[Ir(\mu\text{-dmpz})(CO)_2]_2$ by as much as 3600 cm^{-1} (0.45 eV) relative to the pz$^-$-bridged complex.[28] However, the shorter Ir···Ir separation in the dmpz$^-$-bridged complex (3.25 *vs* 3.51 Å) reinforces the ligand inductive effects, making it difficult to separate the geometric and electronic contributions to this destabilization. The absence of a similar metal−metal interaction may account, at least in part, for a more modest destabilization in the Pt(diimine)$(pyrazolate)_2$ system. The ^{1}MLCT absorption for the dmpz$^-$ complexes is shifted by 600−800 cm^{-1} to the red of related bands in the spectra of pz$^-$ analogues.

The energies of the ^{1}MLCT transitions of the pz* complexes are similar to those observed for the Pt(bpy)X_2 (X = Cl, Br, I) series (*e.g.*, Pt(bpy)Cl_2 in CH_2Cl_2: 394 nm).[5,23] From spectroscopic and electrochemical studies of $Ru(bpy)_2(pz)_2$ and $Ru(bpy)_2Cl_2$, Sullivan and co-workers have suggested that pz$^-$ is a slightly better electron donor than chloride.[18] Lever's electrochemical parametrization of ligands shows that Cl$^-$ (−0.24), Br$^-$ (−0.22), I$^-$ (−0.24), and pz$^-$ (−0.24 V) have very similar E_L values, where the reduction potential of a $[Ru^{III}(bpy)_nL_{6-2n}]^{m+}$ complex is given by[29]

$$E(\mathrm{Ru^{III}/Ru^{II}}) = 2n(0.255) + (6 - n)E_L(L)$$

The Ru^{III}/Ru^{II} reduction potential for $Ru(bpy)_2(pz)_2$ (0.32 V) is 20 mV more negative than the value for Ru(bpy)Cl_2. In agreement with these considerations, the maximum of the MLCT band of $Ru(bpy)_2(pz)_2$ in DMF lies at slightly lower energy (581 nm) than that observed for the dichloro analogue (553 nm).[18]

Emission Spectroscopy. Complexes listed in Table 3 are intensely luminescent in the solid state at room temperature and in glassy solution at 77 K. The variation in color is striking: with pz$^-$ ligands, the emission is green, whereas with methyl-substituted pyrazolate ligands (dmpz$^-$ and tmpz$^-$) it is orange to red. Protonation of the complexes with dmpz$^-$ ligands results in an intense green emission similar to that observed for the deprotonated pz$^-$ derivatives. The emission spectra for 77 K glassy solutions of Pt(bpy)$(pz)_2$, Pt(bpy)$(dmpz)_2$, and their diprotonated forms are shown in Figures 3 and 4, and the solid-state emission spectra for Pt(bpy)$(dmpz)_2$ and Pt(bpy)$(tmpz)_2$ are shown in Figure 5. Although spin−orbit coupling is not negligible in these systems, the relatively long emission lifetimes (70−4000 ns) observed for solid samples are consistent with spin-forbidden transitions. The compounds are weakly luminescent in room-temperature dichloromethane solution, and exceedingly weakly luminescent in methanol solution (Figures 1 and 2). The tmpz$^-$ derivatives are photochemically unstable in solution.

Protonated Complexes. To probe the spectroscopy of the diprotonated pyrazolate complexes, excess trifluoroacetic acid was added to dilute ethanol−methanol (3:1) solutions of these complexes (Figures 3 and 4). Under these conditions, the 77 K emission spectra of the pzH and dmpzH derivatives exhibit characteristic ^{3}LL vibronic structure (Figures 3b and 4b). The emission profiles for $Pt(bpy)(pzH)_2^{2+}$ and $Pt(bpy)(dmpzH)_2^{2+}$ are virtually identical (Figure 4b).[30] These structured spectra are very similar to ^{3}LL luminescence spectra of $Zn(bpy)_3^{2+}$ and $Ir(bpy)_3^{3+}$.[31,32] Moreover, the emission profiles are similar to

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(30) In the solid state, the emission spectrum of $[Pt(dmbpy)(dmpzH)_2](BF_4)_2$ exhibits more complicated structure than that observed in glassy solution. One possible explanation is that there may be more than one distinct cation site in the solid (which has not been crystallographically characterized).

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Table 3. Emission Spectroscopic Data for Bipyridylbis(pyrazolato)platinum(II) Complexes

	emission band maxima (in italics) and shoulders, nm [τ, ns]				
	solid state		glass	room-temperature solution	
compound (emission color)	300 K	10 K	77 K	CH_2Cl_2	methanol
Pt(bpy)(pz)$_2$ (yellow-green)	481, *509*, *549*, 588 [380]	476, *504*, *533*, 575 [3980]	*461*, 484, *495*, *525*, 531, 580, 620	*565* [85]	
Pt(bpy)(dmpz)$_2$ (orange)	*562* [165]	*568* [585]	478, *504*, 540	*630* [4]	*612*
Pt(bpy)(tmpz)$_2$·0.5H_2O (red)	*610* [68]	654, *602*, 570 [140 at 77 K]		*628*[a]	
Pt(dmbpy)(pz)$_2$ (green)	477, *508*, *543*, 595	*478*, *513*, *549*, 595	*460*, 481, *493*, *525*, 570, 620	*556* [32]	
Pt(dmbpy)(dmpz)$_2$ (yelow)	*573* [210]	552, *578* [1820]	*471*, *500*, 535, 585	*619* [7]	*588*
Pt(dmbpy)(tmpz)$_2$·H_2O (orange)	*578* [230]	*590* [430 at 77 K]		*593*[a]	

[a] These solutions are photochemically unstable, and the observed emission may originate from a photoproduct.

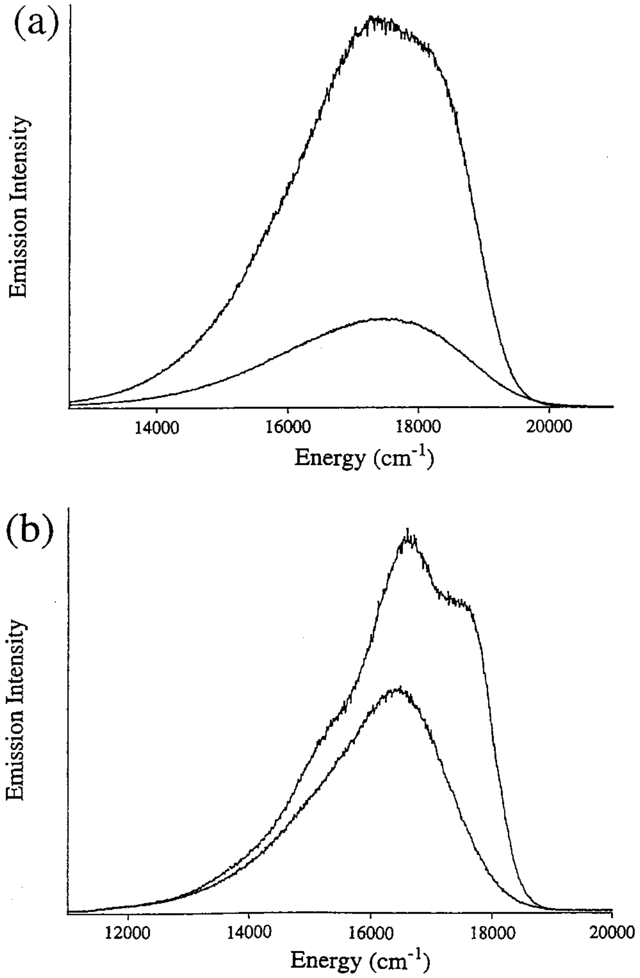

Figure 5. Emission spectra for microcrystalline samples of (a) Pt(bpy)(dmpz)$_2$ and (b) Pt(bpy)(tmpz)$_2$·0.5H_2O at room temperature (lower intensity spectra) and 10 K (λ_{ex} = 457.9 nm).

the structured spectra reported for Pt(bpy)(en)$^{2+}$ in 77 K glassy solution (459, 481sh, 492, 519sh, 529, and 567sh nm *vs* 454, 476sh, 488, 515, 525, 556, 574sh, and 610sh nm for Pt(bpy)(pzH)$_2{}^{2+}$) with comparable Huang−Rhys ratios ($S = I(1,0)/I(0,0) = 1.2-1.3$).[1] Since the green emission from the latter complex clearly originates from a bipyridyl ^{3}LL state, the same assignment is made for the protonated pz$^-$ and dmpz$^-$ derivatives in methanol−ethanol glassy solution. The fact that the emissions from bpy and dmbpy complexes are nearly identical indicates that methyl substituents do not significantly perturb the π/π^* splitting.

In addition to the intense bands near 320 nm, several weak low-energy features can be identified in the 77 K glassy solution excitation spectra of Pt(bpy)(pzH)$_2{}^{2+}$ and Pt(bpy)(dmpzH)$_2{}^{2+}$ (Figures 3b and 4b). Both complexes exhibit weak bands near 420 and 450 nm.[33] A similar pattern has been observed in the room-temperature solution absorption spectrum of Pt(bpy)(en)$^{2+}$ (~420 nm, 10 M^{-1} cm^{-1}; 447 nm, 4 M^{-1} cm^{-1}).[1] The narrow, lower-energy feature overlaps well with the first vibronic feature at 454 nm in the emission spectra of the protonated complexes. Accordingly, we assign this absorption to the lowest energy spin-forbidden singlet−triplet LL transition. The ~420 nm feature is probably a vibronic component of this transition.

Deprotonated Complexes. The emission from the deprotonated dmpz$^-$ and tmpz$^-$ complexes is dramatically different from that of the protonated complexes. An examination of Table 3 reveals that introduction of electron-donating methyl substituents onto the pyrazolate ligands causes the emission maximum to broaden and shift to lower energy. For example, the solid-state room-temperature emission maximum for Pt(bpy)(tmpz)$_2$·0.5H_2O is ~3300 cm^{-1} lower in energy than the most intense feature in the emission spectrum of Pt(bpy)(pz)$_2$ and ~900 cm^{-1} lower in energy than the emission maximum for Pt(bpy)(dmpz)$_2$ (Figure 5). These results are inconsistent with a lowest bipyridyl-centered ^{3}LL excited state, as the energy of that state is relatively insensitive to the nature of the ancillary ligands.[23] Similarly, a ^{3}(d→d) emissive state is ruled out since the ligand field splitting is relatively insensitive to substituents on the pyrazolate ligands. The structured ^{3}LL emission from the protonated derivatives establishes that even the lowest d → d transitions must occur at wavelengths shorter than 450 nm. In addition, similar shapes and energies of the solution, glass, and solid-state spectra for each compound militate against an excimeric emission.[1] In fact, the sensitivity of the emission to the nature of the pyrazolate ligands is similar to that observed for the MLCT absorption bands, and we conclude that the emission from the complexes with dmpz$^-$ and tmpz$^-$ ligands originates from a ^{3}MLCT-[d(Pt)→π^*(bpy)] state.[34] Thus, these results may be understood in terms of the strong σ donor energy level diagram in Scheme 1, whereby increased electron donation by the ancillary ligands to the platinum center stabilizes MLCT states. In accord with

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(33) A weak shoulder also is observed near 380 nm in the excitation spectra of the protonated complexes. Since the deprotonated complexes absorb strongly in this region, the possibility of emission from the residual deprotonated complex cannot be excluded.

(34) The possibility that a Pt(d→p) or ligand-to-metal charge-transfer (LMCT) state is lowest can be rejected on energetic grounds. Vibronic structure associated with the lowest energy triplet intraligand LL transition in platinum bipyridyl complexes originates near 450 nm. However, the lowest energy d → p transitions in platinum(II) complexes typically occur at wavelengths shorter than 250 nm. For example, transitions to the $E_u(^3A_{2u})$ state (D_{4h} symmetry with spin−orbit coupling) of $Pt(NH_3)_4{}^{2+}$ and $PtCl_4{}^{2-}$ occur at <220 nm. Similarly, even in the case of $PtCl_4{}^{2-}$ (with high-energy anionic ligand orbitals), the energy of the $E_u(^3B_{1u})$ LMCT[d_{xy}→p_z] state is greater than 42 000 cm^{-1} (<240 nm) (Mason, W. R. *Inorg. Chem.* **1986**, *25*, 2925. Isci, H.; Mason, W. R. *Inorg. Chem.* **1984**, *23*, 1565. Mason, W. R.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5721. McCaffery, A. J.; Schatz, P. N.; Stephens, P. J. *J. Am. Chem. Soc.* **1968**, *90*, 5730).

these assignments, we find that substitution of methyl groups on the bipyridyl ligand causes the emission energy to increase slightly.

To inhibit protonation of the pyrazolate ligands in solution, excess triethylamine (NEt_3) was added to dilute ethanol−methanol (3:1) solutions of the complexes.[35] The resulting 77 K emission spectra are shifted to lower energy from the spectra of the protonated complexes (Figures 3 and 4). In the case of $Pt(bpy)(pz)_2$, the origin of the emission is shifted by ∼350 cm^{-1} to the red of the ^{3}LL emission from $Pt(bpy)(pzH)_2^{2+}$. Nevertheless, the emission profiles of the protonated and deprotonated pz^- complexes are strikingly similar (Figure 3). This modest perturbation suggests that the emissive state retains considerable ^{3}LL character. In contrast, while the origin of the emission from $Pt(bpy)(dmpz)_2$ is shifted by ∼450 cm^{-1} to the red of the emission from $Pt(bpy)(dmpzH)_2^{2+}$, the emission profile is considerably broader and less structured than that of the protonated complex. Moreover, the emission maximum for $Pt(bpy)(dmpz)_2$ is shifted by ∼2800 cm^{-1} to the red of the most intense feature in the emission spectrum of the protonated complex (Figure 4). We conclude that the emission from $Pt(bpy)(dmpz)_2$ in 77 K glassy solution originates from a lowest ^{3}MLCT state. These results are readily interpreted in terms of Scheme 1. Deprotonation of $Pt(bpy)(dmpzH)_2^{2+}$ stabilizes the lowest ^{3}MLCT excited state below the ligand-centered ^{3}LL excited state. Similarly, introduction of electron-donating methyl groups onto the pyrazolate ligands causes a crossover from a lowest predominantly ^{3}LL excited state in the case of $Pt(bpy)(pz)_2$ to a lowest ^{3}MLCT excited state in the case of $Pt(bpy)(dmpz)_2$.

It is remarkable that crossover between these distinct types of emission occurs over a very narrow energy region, <500 cm^{-1}. Maestri and co-workers have argued that the lowest ^{3}LL and ^{3}MLCT states are heavily mixed in Pt(II) complexes with the cyclometalating 2,6-diphenylpyridyl ligand.[36,37] To determine the extent of LL/MLCT mixing, Yersin and co-workers have recorded highly frequency-resolved and time-resolved absorption and emission spectra of two Pt(II) complexes with pyridyl ligands, $Pt(bpy)_2^{2+}$ and $Pt(2\text{-thpy})_2$ (2-thpyH = 2-(2-thienyl)-pyridine).[38,39] For $Pt(bpy)_2^{2+}$, the zero-field splitting (zfs) of the lowest triplet state is small (<1 cm^{-1}), as expected for a lowest excited state with predominantly LL character. The larger zfs (16 cm^{-1}) of the lowest excited state of $Pt(2\text{-thpy})_2$ suggests slightly greater mixing of MLCT character into the ligand-centered excited state.[39] Related studies of Re(I), Ru(II), Os(II), Rh(III), and Ir(III) complexes with pyridyl ligands support this notion of varying degrees of LL/MLCT mixing in the lowest emissive states.[38,40,41] In a series of careful studies of cyclometalated Rh(III) and Ir(III) complexes, Güdel and co-workers have established that ^{3}LL intensity in absorption and emission is almost entirely attributable to MLCT mixing, as particularly indicated by polarization measurements.[40,42,43] Importantly, the vibronic intensity pattern of the transitions involving the ^{3}LL states is little affected by this mixing. The "intrinsic" intensity of spin-forbidden electronic transitions involving the organic ligand is miniscule, so that a small amount of mixing with much more strongly allowed MLCT transitions completely dominates the observed intensity, but the excited-state distortions, as reflected in the vibronic pattern, remain those characteristic of an LL excited state.[44] We would anticipate perturbation of the vibronic pattern only when the LL and MLCT states are quite close in energy. Myrick and De Armond have reported perturbation of the 77 K glassy solution emission profiles of $Ru(bpy)_2L_2$ complexes when the lowest LL and MLCT excited states are within 3000 cm^{-1} of each other.[45]

The intense bands near 320 and 370 nm in the 77 K excitation spectra of $Pt(bpy)(pz)_2$ and $Pt(bpy)(dmpz)_2$ in ethanol−methanol solution are in good agreement with the room-temperature solution absorption spectra (Figures 3a and 4a). The weak, sharp band at 459 nm in the spectrum of $Pt(bpy)(pz)_2$ overlaps well with the first vibronic feature in the emission spectrum, and we assign this band to the lowest spin-forbidden transition which has predominantly LL character. In contrast, a weak, broad band appears as a shoulder near 464 nm in the excitation spectrum of $Pt(bpy)(dmpz)_2$. This feature overlaps well with the origin of the emission, and we assign this band to the lowest ^{3}MLCT absorption. In both cases, these lowest-energy bands are approximately 20 times as intense as the ^{3}LL absorption in the excitation spectra of the protonated complexes (Figures 3 and 4). This intensity enhancement is attributed to spin−orbit coupling arising from the increased MLCT character of the lowest excited state of the deprotonated complex.

In some instances the assignment of a lowest ^{3}MLCT or ^{3}LL state is ambiguous. For example, the vibronic structure in the solid-state emission spectra of $Pt(bpy)(pz)_2$ and $Pt(dmbpy)(pz)_2$ is red-shifted by ∼600 cm^{-1} from that observed in the spectra of frozen solutions. This result contrasts sharply with the room-temperature solid-state spectrum of $[Pt(bpy)(en)](ClO_4)_2$, which is not shifted with respect to the 77 K glass emission spectrum.[1,2] Thus, while the glassy solution spectra are suggestive of a lowest excited state of predominantly ^{3}LL character, the solid-state spectra indicate increasing ^{3}MLCT contribution. Indeed, the room-temperature emission lifetime for $Pt(bpy)(pz)_2$ (380 ns) is considerably shorter than that of $[Pt(bpy)(en)](ClO_4)_2$ (1400 ns). These results are consistent with absorption spectra that show that the energies of the MLCT bands are sensitive to changes in the molecular environment. This solvent sensitivity can be attributed to differences in charge distribution in the ground and excited states.[46−48] Similar spectral changes are seen in frozen solutions containing less polar solvents. For example,

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(35) In the absence of NEt_3, 77 K glassy solution emission spectra of the nominally pure deprotonated complexes generally show a weak emission component similar to that of the protonated complex. However, the major component of emission for these samples is identical with the single emission observed in the presence of base.

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(44) Güdel and co-workers also have reported a case in which $^3(\pi-\pi^*)$ and ^{3}MLCT states separated by only a few hundred wavenumbers are very weakly mixed.[40] Emission and absorption spectra for the former retain their characteristic sharp vibronic structure, while absorption features of the latter are much broader, presumably because of the expected large distortion along low-frequency metal−ligand deformation coordinates in the MLCT excited state.[57] This example has the peculiarity that the MLCT and LL excitations in question involve different ligands of the complex. Thus, mixing should be intrinsically small, and the situation is not strictly comparable to the compounds of the present study.

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$Pt(bpy)(pz)_2$ in 1:1 dichloromethane−toluene solution at 77 K exhibits the same structured spectrum observed for a methanol−ethanol glass. However, a 1:6 dichloromethane−toluene solution exhibits a broadened and slightly red-shifted emission.

In light of these findings, it is not surprising that the complexes exhibit luminescence rigidochromism.[49] The fluid-solution emission is shifted to lower energy with respect to the emission from rigid media since solvent reorganization tends to stabilize the emissive state. From comparison with related complexes, we conclude that the broad asymmetric emission ($\lambda_{max} \sim 560$ nm) observed for the pz^- derivatives in fluid solution also originates from a ^{3}MLCT excited state. In contrast, both $Pt(bpy)(NH_3)_2^{2+}$ ($\lambda_{max} = 488$ nm, acetonitrile) and Pt(4,4′-di-*tert*-butyl-2,2′-bipyridine)$(CN)_2$ ($\lambda_{max} = 488$ nm, CH_2Cl_2, $\tau = 2.9$ μs) exhibit structured and blue-shifted emission profiles in fluid solution.[50,51] The solution luminescence is weak for the pz* complexes, and the excited-state lifetimes are shorter than 100 ns. Increased ^{3}LL character in the lowest excited state results in longer lifetimes for the complexes with pz^- ligands than those with $dmpz^-$.

^{3}MLCT Emission. The emissive MLCT state in platinum(II) diimine systems does not necessarily have the same parentage as the intense spin-allowed ^{1}MLCT[$d\pi \rightarrow \pi^*$] transition observed in absorption spectra. While the predominantly bipyridyl π^* character of the LUMO is well-established,[6,52−55] the platinum d orbitals comprising the HOMO are less certain. The ordering of the d levels can be expected to depend on the electron donor properties of the ancillary ligands; π donor ligands are expected preferentially to stabilize MLCT[$d\pi \rightarrow \pi^*$] states, whereas σ donor ligands are expected to stabilize MLCT-[$d_{z^2} \rightarrow \pi^*$] states. Consequently, for complexes with strong σ and π donor ligands such as pyrazolates, the exact nature of the emissive state remains an intriguing question. Kaim and coworkers have suggested a lowest ^{3}MLCT[$d_{z^2} \rightarrow \pi^*$] state for platinum(II) diimine bis(alkyl) and bis(aryl) complexes on the basis of spectroscopic studies.[6,56] (The "special" stabilization of d_{z^2} via Pt(5d/6s) mixing in square-planar stereochemistry has been discussed in detail by Vanquickenbourne and Ceulemans.)[57] In those systems, a highest occupied d_{z^2} orbital is consistent with strong σ donation by the alkyl ligands. Interestingly, the reported emission energies for $Pt(bpy)(mesityl)_2$ (solid state, 610 nm; dichloroethane, 663 nm) are comparable to those of the $dmpz^-$ derivatives.

A somewhat different ordering of d levels is expected for $Pt(diimine)X_2$ (X = Cl, Br, I), since π donor interactions destabilize the $d\pi$ levels. Indeed, the emission profiles of the pyrazolate complexes are conspicuously similar to the ^{3}MLCT-[$d\pi \rightarrow \pi^*$] emission spectra of Pt(3,3′-$(CO_2Me)_2$bpy)Cl_2 and Ru-$(bpy)_3^{2+}$.[4,58] For $Pt(dmbpy)(dmpz)_2$ and $Pt(bpy)(tmpz)_2$ (solid state, 10 K), *S* is estimated to be 1.1 and 1.2, respectively. For Pt(3,3′-$(CO_2Me)_2$bpy)Cl_2, *S* is approximately 1.05.[4] In contrast to the $Pt(diimine)(alkyl)_2$ systems, Pt(3,3′-$(CO_2Me)_2$bpy)Cl_2 is not luminescent in fluid solution. As previously suggested,[4] the formally d^7 excited state may be particularly susceptible to quenching *via* strong interaction with solvent and/or nontotally symmetric distortions. It is possible that the susceptibility of ^{3}MLCT[$d\pi(xy,xz,yz) \rightarrow \pi^*$] to quenching distortions will differ from that of ^{3}MLCT[$d_{z^2} \rightarrow \pi^*$] excited states.

It also is noteworthy that the crossover between the ^{3}LL and ^{3}MLCT emission and absorption bands of the pz* complexes occurs over a very narrow energy region, <500 cm^{-1}. According to simple perturbation theory, the magnitude of mixing between LL and MLCT excited states depends on the inverse of their energy separation and upon an interaction matrix element. Regardless of the specific Hamiltonian invoked, the matrix element is expected to increase as the interaction between the π and d orbitals increases. Strong mixing of these transitions in square-planar complexes essentially requires covalent interaction of the relevant d orbitals and the organic π system, so MLCT[$d_{xz,yz} \rightarrow \pi^*$] transitions are the most likely candidates for large mixing.[59] These are also the only MLCT transitions that are likely to exhibit significant electric-dipole-allowed intensity, and therefore account for the observed singlet−singlet parentage MLCT absorption bands. It is important to recognize that these MLCT states are *not* likely to be the lowest-energy ones. The HOMO for PtX_4^{2-} (X = halide) is well-established as d_{xy}.[57] Since π back-bonding of diimine ligands is exclusively out-of-plane, it will preferentially stabilize the d_{xz} and d_{yz} orbitals, so the d_{xy} orbital should remain the highest energy of the $d\pi$ orbitals for Pt(II) complexes of these ligands. In fact, selective destabilization of the d_{xy} orbital due to pyrazolate π donation may be expected, since steric constraints should favor orientation of these planar π donor ligands perpendicular to the square-planar complex.[17] Thus, the weak mixing observed here may be taken as support for a ^{3}MLCT[$d_{xy} \rightarrow \pi^*$] assignment of the emissive level, as this state should mix very little with diimine $\pi-\pi^*$ states. Therefore, very sharp LL/MLCT crossovers can be anticipated. Another possibility, as proposed by Kaim and coworkers,[6,56] is that the filled d_z^2 orbital may become the HOMO for $Pt(diimine)X_2$ when X is a strong σ donor such as an alkyl group. If this orbital is sufficiently destabilized to make ^{3}MLCT-[$d_{z^2} \rightarrow \pi^*$] the lowest excited state, then mixing with diimine LL states will once again be expected to be very weak, and sharp crossovers also would be expected.

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(59) Since we are considering triplet states in the presence of a heavy metal atom (Pt), spin−orbit coupling should of course be considered in a complete treatment. But in the low symmetry of these complexes, the group-theoretical result is simply that, in principle, all triplet states can mix with all other triplet states.