Studies of the Room-Temperature Absorption and Emission Spectra of $[Pt(trpy)X]^+$ Systems

Toni K. Aldridge, Elizabeth M. Stacy, and David R. McMillin*

Department of Chemistry, 1393 Brown Building, Purdue University,
West Lafayette, Indiana 47907-1393

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We report absorption and luminescence data for a series of d^8 complexes with the formula $[Pt(trpy)X]^+$ where trpy denotes 2,2′:6′,2″-terpyridine and X = Cl, NCS, OMe, or OH. Each complex exhibits three or four relatively low-energy absorption maxima in the near-UV and visible regions with extinction coefficients on the order of 1000 $M^{-1}\,cm^{-1}$. Since these energies are well below those of the ${}^1\pi$–π^* transitions of the coordinated trpy ligand, we assign the bands as metal-to-ligand transfer (CT) transitions. At room temperature in deoxygenated acetonitrile each complex, save the chloride derivative, exhibits a broad, unstructured emission signal. The corrected emission maxima (and lifetimes) are 588 nm (3.5 ns), 654 nm (180 ns), and 621 nm (170 ns) for X = NCS, OMe, and OH, respectively. The thiocyanate and hydroxide derivatives also give stable, emissive solutions and significantly enhanced emission lifetimes in methylene chloride. The emissions are assigned to ${}^3d$–π^* CT excited states. Efficient radiationless decay via a low-lying ${}^3d$–d state may explain the fact that there is no detectable emission from the chloride derivative. To obtain additional information about these systems, we have solved the crystal structure of $[Pt(trpy)OMe](BPh_4)$. The crystal symmetry is $P\bar{1}$. The important lattice information includes: $Z = 2$, $a = 10.656(2)$ Å, $b = 11.830(5)$ Å, $c = 14.240(3)$ Å, $\alpha = 110.47(2)°$, $\beta = 92.52(2)°$, and $\gamma = 105.62(3)°$. In the final stage of refinement, $R = 0.056$. The coordination geometry is more-or-less rhombic with slightly shorter bonds to the methoxide oxygen and the central nitrogen of the trpy ligand.

Introduction

Our group has maintained an interest in the photochemical and photophysical properties of four-coordinate complexes capable of achieving an expanded coordination number.[1–5] To date we have concentrated on d^9 and d^{10} systems; however, here we report studies of a series of d^8 platinum(II) complexes. Many of the examples in the literature of platinum(II) complexes that have long-lived excited states and/or exhibit room-temperature luminescence in fluid solution appear to involve ligand-centered, i.e., intraligand, excited states. These include porphyrin complexes,[6] quinolinolate systems,[7] and quaterpyridine complexes,[8] as well as a number of mixed-ligand systems.[9–11] There are also several dinuclear complexes of platinum(II) that are good emitters.[12–15] In the case of $Pt_2(pop)_4^{4-}$ the excitation involves the metal atoms, and the emitting state has been shown to have d–p orbital parentage.[12] Related metal–metal interactions probably occur in oligomeric forms of $Pt(CN)_4^{2-}$ that are emissive in solution.[16] Moreover, there are numerous platinum(II) complexes that are luminescent in the solid state where extended metal–metal interactions are possible.[17]

Emissions from some nominally monomeric platinum(II) centers in the solid state have, on the other hand, been assigned to d–d states. Thus, Preston et al. have assigned a low-temperature emission signal to a d–d excited state of a rhombically distorted form of $PtCl_4^{2-}$.[18] Also, Miskowski et al. have assigned a broad, unstructured emission signal from $PtCl_2(bpy)$ in the solid state or a low-temperature glass to a d–d excited state.[19] However, there are few, if any, reports of d–d emissions from platinum(II) monomers in fluid solution. Some of the d–d excited states of d^8 complexes are unstable with respect to a D_{2d} distortion,[20] and this is likely to facilitate nonradiative decay.[21] The well-known *cis–trans* isomerization of $Pt(gly)_2$ has been attributed to the intermediacy of one such excited state.[22] Axial interactions, analogous to those that occur with copper(II) porphyrins in donor solvents,[5,23] could also induce quenching in solution.

Finally, there are some recent examples of room-temperature emission signals that have been assigned to triplet metal-to-ligand charge-transfer (^{3}CT) excited states.[24–29] In many of these

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* Author to whom correspondence should be addressed.

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systems, however, the authors have stressed that the emitting states are likely to have mixed-parentage. For example, in the case of the diimine dithiolate complexes, the emissive states may have ligand-to-ligand charge-transfer character as well as metal-to-ligand charge-transfer character.[29]

Our initial efforts with the d^8 configuration have focused on complexes of the type $[Pt(trpy)X]^+$ where trpy denotes the tridentate 2,2′:6′,2″-terpyridine ligand. There are several reasons for choosing these systems: (1) One is that the trpy ligand shows a strong preference for a planar geometry and can therefore be expected to discourage the D_{2d} distortions that promote radiationless decay. (2) Because of the extended pi system within the trpy ligand, the complexes are likely to have low-lying CT states with useful photochemical and photophysical properties. (3) The ability to vary the X group affords the possibility of studying a series of related complexes. (4) Finally, there have been a number of studies reported involving binding interactions between platinum(II) terpyridine complexes and particular biological molecules such as DNA[30,31] and proteins.[32] In the following we present studies of the absorption spectra, solution emission spectra and luminescence lifetimes of several platinum(II) terpyridine complexes as well as the structure of a methoxide derivative, $[Pt(trpy)OMe]BPh_4$.

Experimental Section

Materials. We used reagent grade materials as received. The chemicals $NaBF_4$, KPF_6, $NaBPh_4$, NaSCN, and 2,2′:6′,2″-terpyridine came from Aldrich Chemical Co. Fisher Chemical Co. supplied the $AgNO_3$ while K_2PtCl_4 was a gift from Johnson Matthey. We synthesized $[Pt(trpy)Cl]Cl{\cdot}2H_2O$ by literature procedures,[33,34] and we purchased some material from Aldrich. Baxter Scientific supplied fluorescent grade methanol, acetonitrile and methylene chloride for use in fluorescence measurements.

Methods. We determined quantum yields by the method of Parker and Rees.[35] As a reference standard, we used $[Ru(bpy)_3]^{2+}$ which has an emission quantum yield of 0.062 in acetonitrile as reported by Meyer and co-workers.[36] The solvent was CH_3CN except for $[Py(trpy)OMe]^+$ where we used 90:10 $CH_3CN/MeOH$ or neat MeOH. We degassed the solvents by three freeze–pump–thaw cycles. To obtain emission spectra, we excited all solutions at 340 nm and filtered the emission through a 520 or a 450-nm long-pass filter.

The 337-nm line from a nitrogen laser served as the excitation source for the lifetime measurements, and a 337-nm band-pass filter removed stray light from the beam. We analyzed the lifetime data with the program TAU.MOD developed in this laboratory or with a convolution program developed in the laboratory of Dr. Fred Lytle from Purdue University. Preparative procedures for the platinum complexes follow.

$[Pt(trpy)OH]BF_4$. We began with 50 mg of $[Pt(trpy)Cl]Cl{\cdot}2H_2O$ in 20 mL of deionized H_2O. To this we added 1 mL of 6 M NaOH and warmed the solution while stirring for 30 min. Crystallization occurred after the addition of excess aqueous $NaBF_4$ with cooling. We collected the crystals on a filter funnel and dried them under a vacuum. Anal. Calcd: C, 33.90; H, 2.10; N, 7.91. Found: C, 33.74; H, 2.10; N, 7.92.

$[Pt(trpy)NCS]BF_4{\cdot}H_2O$. The procedure was essentially that of Intille.[33] The first step was the dropwise addition of a small excess of aqueous NaSCN to $[Pt(trpy)Cl]Cl{\cdot}2H_2O$ dissolved in a minimum of distilled water. The addition of aqueous $NaBF_4$ produced a precipitate that we filtered, dried, and recrystallized from CH_3CN/H_2O. The infrared spectrum of the product gave a thiocyanate band at 2105 cm^{-1}. Anal. Calcd: C, 32.52; H, 1.93; N, 9.76. Found: C, 32.40; H, 1.90; N, 9.47.

$[Pt(trpy)OMe]BPh_4$. We warmed 20 mg of $[Pt(trpy)OH]BF_4$ in 20 mL of methanol for 2 h. We then added 2 equiv of $NaBPh_4$ dissolved in MeOH. Allowing this mixture to stand at room temperature for 1 h produced a red precipitate. Yellow crystals deposited later. The red crystals analyzed as the methoxide adduct. Anal. Calcd: C, 61.69; H, 4.53, N, 5.40. Found: C, 61.49; H, 4.30; N, 5.29.

$[Zn(trpy)_2](ClO_4)_2$. We precipitated a white solid from an aqueous solution containing zinc acetate and 2 equiv of the trpy ligand by the addition of $NaClO_4$. After washing the solid with cold water, we recrystallized the material from hot water.

Instrumentation. A Perkin-Elmer Lambda 4C UV/vis spectrophotometer provided absorption data, and an SLM-Amino SPF-500C spectrophotometer gave the steady-state emission spectra. We obtained some of the lifetime data with an EG&G Princeton Applied Research Model 2100 nitrogen-pumped dye laser in conjunction with a Tektronix TDS 520 digitizing oscilloscope and TEKDIG data handling software. For other measurements we used a PTI Laser Inc. Model PL 2300 nitrogen pulsed laser system. With this system a Tektronix DSA 602 signal analyzer captured the data, and an IBM PS/2 Model 70 computer controlled the experiments via a Keithly-DAS Series 500 interface.

Crystallography. The data came from a plate of $[Pt(trpy)OMe]BPh_4$ of approximate dimensions of 0.17 × 0.11 × 0.04 mm mounted on a glass fiber. We collected data with Cu $K\alpha$ radiation ($\lambda = 1.541\,84$ Å) on an Enraf-Nonius CAD4 computer-controlled, κ-axis diffractometer equipped with a graphite crystal, incident beam monochromator. A least-squares refinement of data from the setting angles of 25 reflections (in the range $19° < \theta < 28°$ measured by the computer-controlled diagonal slit method of centering) gave cell constants and an orientation matrix. The ω scans of several intense reflections served to check on crystal quality. The width at half-height was 1.37° with a take-off angle of 6.0°. The temperature was 293 ± 1 K, and we used the ω–2θ scan technique. The scan rate varied from 2 to 16°/min (in ω). We collected a total of 4311 unique reflections and used the Patterson heavy-atom method to locate the Pt atom. Succeeding difference Fourier syntheses permitted identification of the remaining atoms. Although we located the hydrogen atoms and added them to the structure factor calculations, we did not refine their positions.

Results

For the most part the compounds are stable in acetonitrile solution. In the case of the methoxide derivative the absorption spectrum slowly evolves into that of the hydroxide complex. Since the addition of 10% methanol as a cosolvent suppressed the decomposition reaction, we recorded the spectral data for the methoxide complex in the mixed solvent. In methanol the chloride and hydroxide derivatives underwent partial solvolysis because each gave a weak emission and an excitation spectrum that matched those of the methoxide complex. The other type of decomposition we observed was photodecomposition of the methoxide complex in methylene chloride. The photochemistry apparently involves the solvent because the absorption spectrum of the photoproduct shows evidence of formation of the chloride complex. Photoinduced reduction of solvent is a known reaction of platinum(II) complexes dissolved in chlorocarbons.[24]

Absorption Spectra. Figure 1 presents the absorption spectra of $[Pt(trpy)Cl]^+$, $[Pt(trpy)NCS]^+$, and $[Pt(trpy)OMe]^+$ in acetonitrile at room temperature. Table 1 contains the wave-

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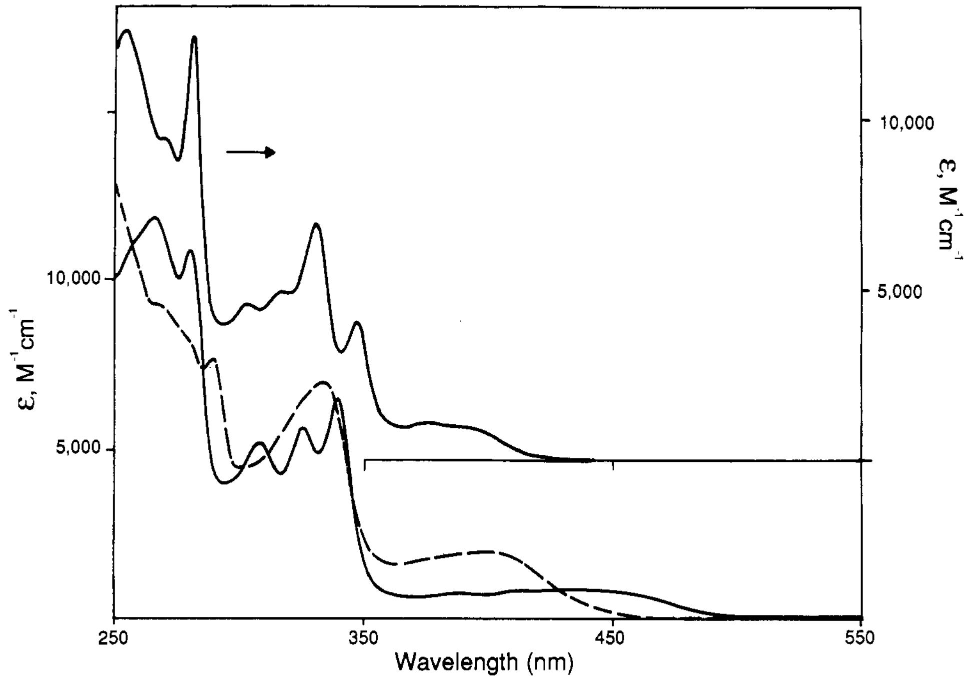

Figure 1. Room-temperature absorption spectra in acetonitrile. [Pt(trpy)OH]$^+$ (—) and [Pt(trpy)NCS]$^+$ (- - -). Offset spectrum: [Pt(trpy)Cl]$^+$.

Table 1. Absorption Data in Acetonitrile at Room Temperature

complex	λ_{max},nm (ϵ, M^{-1} cm^{-1})								
[Pt(trpy)Cl]$^+$		280 (25000)	303 (9200)	317 (10000)	330 (14200)	347 (8200)	377 (2200)	390 sh (1960)	
[Pt(trpy)NCS]$^+$		289 (15400)		327 sh	334 (14000)		373 sh (3500)	387 sh (3800)	400 (4000)
[Pt(trpy)OH]$^+$	273	280 (21900)	308 (10450)	325 (11300)	339 (13100)	388 (1500)	415 (1650)	436 (1600)	~457 sh
[Pt(trpy)OMe]$^{+\,a}$	273 sh	278 (22200)	310 (10350)	327 (10100)	339 (10550)	380 (1420)	420 (1020)	~450	~470 sh
[Zn(trpy)$_2$]$^{2+}$		282	308 sh	321	334				

[a] Solvent contained 10% methanol.

Table 2. Emission Data at 30 °C

	solvent					
	CH$_3$CN^a				CH$_2$Cl$_2$^{b}	
compound	λ_{max},^{c} nm	τ, ns	Φ	k_r,^{d} s^{-1}	λ_{max},^{c} nm	τ, ns
[Pt(trpy)OMe]$^+$	654	180	0.0015	8.3×10^3		
[Pt(trpy)OH]$^+$	621	170	0.0021	1.2×10^4	610	2000
[Pt(trpy)NCS]$^+$	588	3.5	0.000094	2.7×10^4	594	130

[a] With 10% MeOH for the methoxide system. [b] With 5% CH$_3$CN for the hydroxide system. [c] From the uncorrected spectrum. [d] Estimated from Φ/τ.

lengths of the absorption maxima of these compounds as well as [Pt(trpy)OH]$^+$ and [Zn(trpy)$_2$]$^{2+}$. When dissolved in acetonitrile, the absorbance of each platinum complex follows Beer's law and is consistent with dissolution into monomeric ions.

In accordance with the spectrum of [Zn(trpy)$_2$]$^{2+}$, each platinum complex should exhibit a relatively sharp transition at ca. 280 nm and a pair of maxima in the range of 320–340 nm due to intraligand π–π^* transitions of the coordinated trpy ligand. Ratilla and Kostić assigned the bands of the imidazole derivative at 328 and 342 nm as CT transitions,[32] but in view of the results in Table 1 these bands more likely represent π–π^* transitions. The absorption bands in Table 1 with $\lambda_{max} > 350$ nm appear to be too low in energy to be π–π^* transitions and too intense ($\epsilon \geq$ 1000 cm^{-1}) to be d–d transitions. They are most likely metal-to-ligand charge-transfer (CT) transitions analogous to those identified in the spectra of platinum(II) bipyridine complexes.[37] These bands generally shift to lower energy when the solvent is methylene chloride (Table 2), consistent with charge transfer character.[37,38]

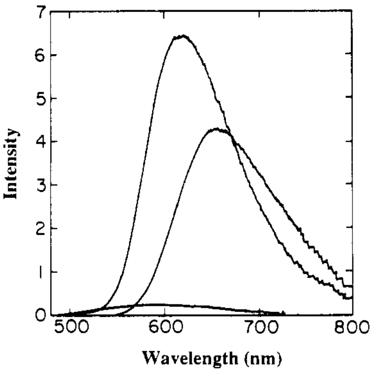

Figure 2. Corrected emission spectra run at 30 °C. In order of decreasing intensity the spectra are from [Pt(trpy)OH]$^+$, [Pt(trpy)OMe]$^+$, and [Pt(trpy)NCS]$^+$. The solvent was acetonitrile except in the case of the methoxide complex where the solvent contained 10% methanol.

Emission Spectra. Three of the four derivatives gave broad, structureless emission spectra in acetonitrile at 25 °C. The exception was the chloride complex, which was nonemissive. Figure 2 includes the emission spectra of the thiocyanate, hydroxide, and methoxide complexes. Table 2 lists the corrected emission maxima, which were independent of the platinum concentration over the range 10–500 μM. In each case the excitation spectrum matched the absorption spectrum of the solution.

The hydroxide and the thiocyanate complexes also emit in methylene chloride, and the emission maxima occur at practically the same wavelengths as in acetonitrile (Table 2). The methoxide complex was the only complex that would emit in room-

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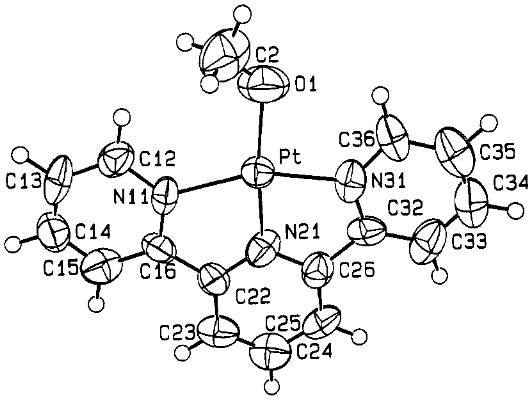

Figure 3. ORTEP diagram of [Pt(trpy)OMe]$^+$ with the atom-numbering scheme.

Table 3. Crystallographic data for [Pt(trpy)OMe](BPh$_4$)

$PtON_3C_{40}BH_{34}$	fw = 778.64
$a = 10.656(2)$ Å	space group: $P\bar{1}$ (No. 2)
$b = 11.830(5)$ Å	$T = 293$ K
$c = 14.240(3)$ Å	$\lambda = 1.541\ 84$ Å
$\alpha = 110.47(2)°$	$\rho_{calc} = 1.616$ g cm^{-3}
$\beta = 92.52(2)°$	$\mu = 85.51$ cm^{-1}
$\gamma = 105.63(3)°$	transm coeff = 1.000–0.508
$V = 1600(2)$ Å^3	$R(F_o) = 0.056$
$Z = 2$	$R_w(F_o) = 0.061$

temperature methanol solution. In this case there was a slight shift in the wavelength maximum to 645 nm in the corrected spectrum. The complexes generally give $^3\pi$–π^* emission from the coordinated trpy ligand in a low-temperature alcohol glass. However, we have focused on the room-temperature emission and have not excluded the possibility that aggregation/microcrystallite formation complicates the results in low-temperature rigid matrices.

Photophysical Data. Table 2 also contains the emission quantum yields and lifetimes, measured at 30 °C under nitrogen. The emission yield of [Pt(trpy)OMe]$^+$ was 60% smaller in pure methanol than in 90:10 CH$_3$CN/MeOH solution. The lifetimes were independent of the platinum concentration in the range investigated (10–100 μM). Residual plots showed the decays to be monoexponential.

In methylene chloride, the thiocyanate and hydroxide complexes exhibited much longer emission lifetimes. Consistent with the reduced emission yield in methanol versus acetonitrile, the emission lifetime of the methoxide complex dropped to 25 ns in pure methanol.

Structure of [Pt(trpy)OMe]BPh$_4$). The lattice contains discrete cations and discrete anions. Figure 3 is an ORTEP plot of the cation complete with the atom-numbering scheme. Table 3 is a compilation of the crystallographic data, and Table 4 contains the coordinates of all nonhydrogen atoms. Table 5 supplies selected bond distance and bond angle data. The coordination geometry is essentially square planar; atom N(21) exhibits the maximum deviation of 0.071 Å from the best plane through the platinum, oxygen, and three nitrogen atoms. The trpy ligand is only slightly ruffled with the maximum deviation of any atom from the best plane through the ligand being 0.01 Å (C(35)). The individual pyridine rings make dihedral angles of 3.56 (N(11) ring), 1.56 (N(21) ring), and 6.84° (N(31) ring) with the mean plane of the platinum atom and the four donor atoms. The dihedral angle between the same reference plane and the Pt–O(1)–C(2) plane is 148.40°.

The bond between platinum and the central nitrogen of the trpy ligand is significantly shorter than the bond to either of the other two nitrogens. This is true of metal–terpyridine complexes in general due to a geometric constraint imposed by the ligand.[39–41] For the same reason the N–Pt–N bite angles are only 79.1(0.6) and 80.5(0.7). The Pt–O distance is 2.00(1) Å and compares with Pt–O distances of 1.990 Å in [(DPPE)Pt(Me)(OMe)]$^+$, 2.037 Å in (DPPE)Pt(OMe)$_2$, and 2.027 Å in [Pt(NH$_3$)$_2$(mcyt)(OH)]$^+$.[42]

Table 4. Positional Parameters and Their Estimated Standard Deviations for [Pt(trpy)OMe] (BPh$_4$)

atom	x	y	z	B,[a] Å^2
Pt	0.00656(7)	0.37780(7)	0.02487(6)	3.96(1)
O(1)	0.185(1)	0.405(1)	–0.018(1)	8.0(4)
N(11)	0.031(1)	0.470(1)	0.1829(8)	4.2(3)
N(21)	–0.173(1)	0.351(1)	0.047(1)	5.2(4)
N(31)	–0.086(1)	0.269(1)	–0.1197(9)	4.8(3)
C(2)	0.290(2)	0.417(2)	0.033(2)	8.6(7)
C(12)	0.148(1)	0.535(1)	0.243(1)	5.1(4)
C(13)	0.148(2)	0.596(2)	0.345(1)	6.6(5)
C(14)	0.034(2)	0.595(2)	0.380(1)	5.8(5)
C(15)	–0.083(2)	0.530(1)	0.319(1)	5.8(5)
C(16)	–0.086(1)	0.467(1)	0.216(1)	4.4(4)
C(22)	–0.203(1)	0.396(1)	0.142(1)	4.5(4)
C(23)	–0.332(1)	0.373(1)	0.158(1)	5.6(5)
C(24)	–0.429(2)	0.307(1)	0.079(1)	6.1(5)
C(25)	–0.402(1)	0.260(1)	–0.021(1)	5.6(5)
C(26)	–0.271(2)	0.281(1)	–0.034(1)	4.8(4)
C(32)	–0.219(1)	0.240(1)	–0.129(1)	4.5(4)
C(33)	–0.292(2)	0.162(2)	–0.226(1)	6.7(5)
C(34)	–0.228(2)	0.118(2)	–0.307(1)	7.2(6)
C(35)	–0.095(2)	0.151(2)	–0.293(1)	7.3(6)
C(36)	–0.020(2)	0.231(1)	–0.200(1)	5.9(5)
C(101)	0.324(1)	0.827(1)	0.681(1)	3.6(4)
C(102)	0.460(1)	0.861(1)	0.714(1)	4.3(4)
C(103)	0.534(1)	0.779(1)	0.682(1)	4.7(4)
C(104)	0.476(1)	0.659(1)	0.612(1)	5.4(5)
C(105)	0.346(1)	0.623(1)	0.579(1)	4.9(4)
C(106)	0.269(1)	0.704(1)	0.614(1)	4.7(4)
C(111)	0.088(1)	0.869(1)	0.662(1)	3.9(4)
C(112)	–0.003(1)	0.782(1)	0.688(1)	4.7(4)
C(113)	–0.135(1)	0.725(1)	0.640(1)	5.2(5)
C(114)	–0.175(1)	0.753(1)	0.560(1)	5.2(5)
C(115)	–0.086(1)	0.837(1)	0.529(1)	5.1(5)
C(116)	0.046(1)	0.893(1)	0.581(1)	4.2(4)
C(121)	0.235(1)	0.977(1)	0.844(1)	4.0(4)
C(122)	0.316(1)	0.959(1)	0.915(1)	4.1(4)
C(123)	0.310(2)	1.007(2)	1.017(1)	5.6(5)
C(124)	0.223(2)	1.067(2)	1.055(1)	5.8(5)
C(125)	0.138(2)	1.087(2)	0.991(1)	6.0(5)
C(126)	0.144(1)	1.039(1)	0.886(1)	4.9(4)
C(131)	0.319(1)	1.056(1)	0.697(1)	3.9(4)
C(132)	0.370(1)	1.047(1)	0.607(1)	5.1(5)
C(133)	0.431(2)	1.148(2)	0.584(1)	6.1(5)
C(134)	0.443(2)	1.271(2)	0.648(1)	6.4(5)
C(135)	0.396(2)	1.288(2)	0.739(1)	6.0(5)
C(136)	0.331(1)	1.181(1)	0.760(1)	4.9(5)
B(100)	0.242(2)	0.931(1)	0.722(1)	3.7(4)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent temperature factor defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Discussion

Electronic Spectra. The absorption bands that fall below the lowest energy $^1\pi$–π^* absorption bands ($\lambda_{max} > 350$ nm) could have a number of origins. Thus, they could have ^{1}n–π^*,[43] metal-to-ligand CT,[19,25,29] interligand CT,[38,44] or $^3\pi$–π^* character.[17,45] Of course there could be transitions with mixed orbital parentage as well, and some of the structure within the absorption envelope

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Table 5. Bond Distances (Å) and Bond Angles (deg) for [Pt(trpy)OMe(BPh$_4$)]^a

Bond Distances			
Pt-O(1)	2.00(1)	C(14)-C(15)	1.35(2)
Pt-N(11)	2.10(1)	C(15)-C(16)	1.39(2)
Pt-N(21)	1.92(1)	C(16)-C(22)	1.44(2)
Pt-N(31)	2.04(1)	C(22)-C(23)	1.37(2)
O(1)-C(2)	1.26(2)	C(23)-C(24)	1.34(3)
N(11)-C(12)	1.34(2)	C(24)-C(25)	1.41(3)
N(11)-C(16)	1.35(2)	C(25)-C(26)	1.39(2)
N(21)-C(22)	1.36(2)	C(26)-C(32)	1.46(2)
N(21)-C(26)	1.36(2)	C(32)-C(33)	1.41(2)
N(31)-C(32)	1.35(2)	C(33)-C(34)	1.38(3)
N(31)-C(36)	1.38(2)	C(34)-C(35)	1.35(3)
C(12)-C(13)	1.38(3)	C(35)-C(36)	1.38(3)
C(13)-C(14)	1.34(3)		
Bond Angles			
O(1)-Pt-N(11)	108.2(6)	C(12)-N(11)-C(16)	123(2)
N(11)-Pt-N(31)	159.3(6)	Pt-N(21)-C(22)	121(1)
O(1)-Pt-N(21)	171.6(7)	Pt-N(21)-C(26)	118(1)
N(21)-Pt-N(31)	80.5(7)	N(21)-C(26)-C(32)	113(2)
O(1)-Pt-N(31)	92.5(7)	C(25)-C(26)-C(32)	27(2)
Pt-O(1)-C(2)	127(2)	N(31)-C(32)-C(26)	115(2)
N(11)-Pt-N(21)	79.1(6)	N(31)-C(32)-C(33)	118(2)
Pt-N(11)-C(12)	125(1)	C(26)-C(32)-C(33)	127(2)
Pt-N(11)-C(16)	111(1)		

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits.

could be vibronic in nature. As discussed above, metal-to-ligand CT absorption band assignments seem most feasible here. Within the context of perturbation theory, the important factors determining the energies and intensities of CT transitions are normally (i) the energy gap between the donor and acceptor orbitals, (ii) the extent of the orbital overlap, and (iii) the average displacement of the transferred electron.[46–48]

When opposite pairs of donor atoms define the x- and y-axes, the highest occupied orbital of the Pt(II) center in a planar coordination geometry is frequently the $5d_{z^2}$ orbital.[12,49] (Although in C_{2v} symmetry the 2-fold axis normally defines the z-direction, in the trpy complexes we take the y-axis to be along the Pt–N(21) bond and the z-axis to be normal to the plane of coordination in order to retain the correspondence with idealized D_{4h} symmetry.) Thus, when the ligands are strictly σ-donors, overlap considerations predict that the d_{z^2} orbital will be the second highest energy orbital and therefore the highest occupied orbital in a d^8 system.[50] In addition, π-acceptor ligands can preferentially stabilize some of the other d orbitals.[12] On the other hand, in planar Pt(II) complexes a second-order Jahn–Teller interaction with the 6s orbital tends to stabilize the $5d_{z^2}$ orbital and may change the relative energies of the 5d orbitals.[51]

Since the trpy ligand has low-lying π^* orbitals, π-back-bonding interactions are likely to be important. The π^* orbitals are either symmetric (χ) or antisymmetric (ψ) with respect to the 2-fold rotation axis.[52] The AM1 calculations of Hecker et al. suggest that a χ orbital is the lowest energy unoccupied orbital of the trpy ligand but that a ψ orbital is less than 0.5 eV to higher energy.[40] However, according to the extended Hückel calculations of Collin et al., the antisymmetric ψ orbital occurs at lower energy.[53] This disparity may reflect the different methods and/or different assumptions about bond lengths, etc. The safe conclusion is probably that there are two low-lying π^* orbitals with not greatly different energies. The χ orbital has a nodal plane passing through the yz plane and is capable of interacting with the d_{xz} orbital, while the ψ orbital can only interact with d_{yz}. In view of the expected π-back-bonding interactions and the σ-bonding interactions described above, we arrive at the energy level scheme depicted in Figure 4. In this diagram the choices regarding the relative energies of d_{xz} versus d_{yz} and d_{xy} versus d_{z^2} are somewhat arbitrary. We have indicated d_{xy} as the highest occupied orbital because this choice is probably more consistent with the luminescence results; vide infra.

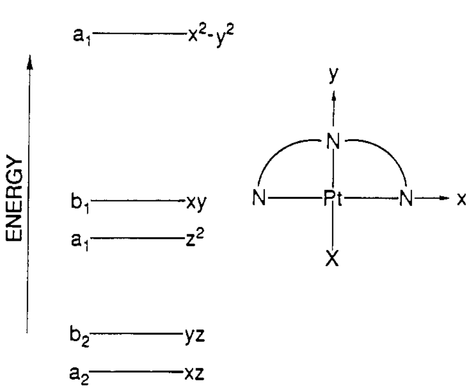

Figure 4. Possible d orbital energy level scheme for the [Pt(trpy)X]$^+$ system. According to this diagram the d_{xy} orbital would be the HOMO for the d^8 system.

A CT transition occurs by the electric dipole mechanism either as a directly allowed transition or as a vibronic transition. According to the scheme in Figure 4, CT transitions could occur from any of the filled d orbitals to the χ or ψ orbitals. The transitions from $d_{xy} \rightarrow \chi$ and $d_{z^2} \rightarrow \psi$ are symmetry allowed but z polarized, while the $d_{xy} \rightarrow \psi$ and $d_{z^2} \rightarrow \chi$ transitions can occur by a vibronic mechanism. Thus, even if we discount the possibility of any type of vibrational structure in the experimental spectrum, we could rationalize the four, low-energy bands observed in the spectrum of the hydroxide derivative. The intensities are not high ($\epsilon < 4000$), but none of the proposed transitions is y polarized. Theory shows that only CT transitions polarized along the metal–ligand axis benefit from the charge-transfer term, usually the dominant factor in the expression for the transition dipole moment of an intense CT absorption.[47,48,54] The y-polarized CT transitions are $d_{yz} \rightarrow \psi$ and $d_{xz} \rightarrow \chi$. According to the proposed energy level diagram in Figure 4, both should occur at higher energy. The relatively intense band that occurs at about 310 nm in the spectrum of the hydroxide or the methoxide complex may be attributable to one of the y-polarized CT bands. The band at 303 nm in the spectrum of the chloride complex may have a similar origin.

We can only speculate at this time why many of the CT transitions shift to lower energy in the case of the hydroxide and methoxide complexes. To the extent that the monodentate ligand can be regarded as a spectator ligand in the CT process, the coulombic effect may be important.[55] Thus, the shorter metal-to-oxygen bond length should allow for easier generation, at least in the formal sense, of a platinum(III) center. Alternatively, π-donation effects and/or the influence of ligand-to-ligand CT states may be important.

Although these absorption bands shift to lower energy in the less polar solvent methylene chloride, the bands appear to be less solvent sensitive than those of Pt(bpy)Cl$_2$[37] or those of a mixed-ligand catecholate complex.[38] The explanation may be a smaller polarity change in the excited states of the trpy systems. Note that when the charge shifts onto the trpy ligand, the shift in the electron density is to a large extent toward the outer pyridines

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of the trpy group. This part of the charge migration has little effect on the dipole moment.

Emission Studies. The emission energies and the band shapes, which are devoid of resolved vibrational structure, strongly suggest that the emissions do not originate from $^3\pi$–π^* states. The broad band shapes are more consistent with emission from ^{3}d–d, ^{3}CT or excimer states. Excimer emission can probably be discounted because of the lack of a concentration dependence. It is also unlikely that the emission originates in a ^{3}d–d state because this kind of emission is extremely rare from a platinum(II) systems. Populating a ^{3}d–d state involves promoting an electron into the metal–ligand antibonding $d_{x^2-y^2}$ orbital. As a result these excited states are subject to strong distortions and are likely to be substitution active and short-lived. In accord with the presence of low-lying charge-transfer bands in the absorption spectra, the emission most likely comes from a ^{3}CT state. The excitation could involve ligand-to-ligand charge transfer as well as metal-to-ligand charge transfer, but the lack of a significant solvent dependence suggests that there is minimal ligand-to-ligand character. The fact that a metal-to-ligand CT state is not expected to have a large dipole moment in these mixed-ligand trpy complexes is consistent with the small solvent dependence of the emission.

As discussed above, the lowest energy CT state is likely to involve excitation from the d_{xy} or the d_{z^2} orbital. If there were a hole in the d_{z^2} orbital, the excited state would be likely to be quenched by solvent and other nucleophiles that could attack the axial positions.[5] In view of the lifetimes observed in CH_3CN solution, the excitation more likely originates in the d_{xy} orbital. Either way, the emissive transition is not likely to be strongly orbitally allowed. In point of fact, the estimated radiative rate constants in Table 2 are on the order of 10^4 s^{-1} whereas the orbitally allowed emission from ^{3}CT states in analogous Os(II) systems are an order of magnitude larger.[56]

The data in Tables 1 and 2 suggest that the luminescence lifetime increases as the energy of the lowest energy CT excited state decreases. This is contrary to expectations based on the energy gap law[57] and may reflect the influence of another excited state. In their studies of cyclometalated platinum(II) complexes, Maestri et al. have found evidence for a thermally activated decay process in which the emissive CT excited state converts to the ground state via a short-lived ^{3}d–d excited state.[58] A similar mechanism can explain the lifetime trends in our systems if the deactivating state becomes less accessible as the ^{3}CT state drops to lower energy. Preliminary studies of the temperature dependence of the lifetime of the photoexcited state of [Pt(trpy)OMe]$^+$ in alcohol solution indicate that there is a thermally activated decay process with a barrier height of ca. 950 cm^{-1}.

Conclusions

Our analysis indicates that [Pt(trpy)X]$^+$ systems exhibit several metal-to-ligand CT absorption bands in the visible and near-UV regions of the spectrum. We have also established that the thiocyanate, hydroxide, and methoxide derivatives exhibit luminescence in room-temperature acetonitrile solution. In view of the broad band shape, modest solvent dependence, and the lack of concentration dependence, we assign the emission to a ^{3}d–π^* CT state. The observation of submicrosecond lifetimes for the emissive states in a donor solvent is quite interesting because of the open coordination sites present on the platinum center and the expectation of enhanced electrophilicity in a typical metal-to-ligand CT excited state. In terms of applications, these findings suggest that luminescence could be a useful tool in binding studies involving platinum(II) terpyridines and biological macromolecules.

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Supplementary Material Available: Listings of anisotropic thermal parameters for [Pt(trpy)OMe]BPh_4 (2 pages). Ordering information is given on any current masthead page.

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