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Remarkable substituent effects on the photophysics of Pt(4′-X-trpy)Cl$^+$ systems (trpy = 2,2′; 6′,2″-terpyridine)

Denise K. Crites, Corey T. Cunningham, David R. McMillin *

Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393, USA

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Abstract

In view of the interest in probing the binding interactions that occur between platinum complexes and biological macromolecules, the aim of this work has been to develop systems that exhibit enhanced excited-state lifetimes and emission yields in fluid solution. The investigation focuses on a series of complexes of the type Pt(4′-X-T)Cl$^+$ where 4′-X-T denotes a 4′-substituted derivative of 2,2′; 6′,2″-terpyridine. In all cases the counterion is the non-coordinating ion tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. The substituents employed include electron-withdrawing groups like CN and SO_2Me as well as electron-donating groups like SMe and NMe_2. Within the series of complexes, the first reduction wave ranges over about 0.7 V in DMF. Although the process probably entails ligand reduction, the acceptor orbital appears to have some platinum $6p_z$ character. Even though electron-donating substituents destabilize the reduced form of the ligand, all substituents induce a red-shift in the charge-transfer (CT) absorption band system that occurs around 400 nm. Furthermore, there is generally an increase in the CT absorption intensity, the emission lifetime and the emission quantum yield in methylene chloride. Thus, at room temperature, the complex with the terpyridine ligand itself is a very poor emitter with an emission lifetime of 10 ns or less, while the Pt(4′-SMe-T)Cl$^+$ and Pt(4′-NMe_2-T)Cl$^+$ systems exhibit lifetimes of 140 ns and 1.9 μs, respectively. With the electron-donating substituents in particular, the lifetime enhancement reflects a configuration interaction between the original CT state and an intraligand charge-transfer excited state. Substituents also influence a thermally activated pathway to radiationless decay.

Keywords: Luminescence; Photophysics; Platinum complexes; Terpyridine complexes

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1. Introduction

The binding interactions that complexes of platinum(II) with polypyridine ligands undergo with DNA [1–5] and globular proteins [6] have helped fuel interest in these systems. In addition, the platinum(II) materials themselves show interesting electronic properties in the solid state including photoluminescence [7–10]. The observation of photoluminescence in fluid solution is a rarer phenomenon, but there are some recent reports of emission from monomeric platinum(II) polypyridine complexes [11–15]. In the present context, the most relevant systems are Pt(trpy)OH$^+$, where trpy denotes the 2,2′; 6′,2″-terpyridine ligand [13], and a Pt(4′-R-trpy)Cl$^+$ series, where R = C_6H_4OMe-*p*, C_6H_4Me-*p*, C_6H_4Br-*p* or C_6H_4CN-*p* [15]. When the emission originates in a metal-to-ligand charge-transfer (CT) excited state, the intensity and the lifetime vary dramatically with the solvent probably in large part because of the availability of open coordination sites at the metal center [13]. Reductive quenching of the CT state is also common [5,15]. For Pt(trpy)L^{n+} systems, the luminescence properties are particularly sensitive to the nature of ligand L [13,15], due perhaps to a variation in the efficiency of radiationless decay via a thermally accessible d–d excited state [13,16]. In the case of the Ru(trpy)$_2^{2+}$ system, which shares some properties in common with platinum(II) terpyridines, the systematic exploration of substituent effects has provided useful insights into the photochemistry and photophysics [17–19]. Those reports provided the impetus for the following spectroscopic and electrochemical studies of a series of complexes of the type Pt(4′-X-T)Cl$^+$, where 4′-X-T denotes the trpy derivative with substituent X in the 4′ position. The most intriguing finding is that the introduction of an electron-donating group

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* Corresponding author. Fax: +1 317 494 0239; e-mail: mcmillin@purdue.edu

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can dramatically enhance the emission yield and the lifetime as a consequence of the admixture of intraligand excited state character that occurs in the emitting state.

2. Experimental

2.1. Materials

Aldrich supplied 2,2′:6′,2″-terpyridine, 4′-chloro-2,2′:6′,2″-terpyridine, potassium tert-butoxide, 2-acetyl pyridine, carbon disulfide, methyl iodide, ammonium acetate, methyl magnesium bromide, selenium dioxide, potassium cyanide, *m*-chloroperoxybenzoic acid, 4-morpholineethanesulfonic acid (MES), 3,5-bis(trifluoromethyl)bromobenzene, hexamethylphosphoramide (HMPA) and tetrabutylammonium hexafluorophosphate (TBAH). The $ZnCl_2$ came from Mallinckrodt. Janssen Chimica supplied boron trifluoroetherate. Baxter supplied B&J brand high purity solvents for spectroscopic measurements (acetonitrile, *N,N*-dimethylformamide and methylene chloride). Other solvents were reagent grade. The K_2PtCl_4 was a gift from Johnson Matthey. The purity of most materials was satisfactory as received. In the case of TBAH, a series of three recrystallizations from ethanol gave a pure compound.

2.2. Methods

The methods reported by Potts et al. provided routes to the trpy derivatives 4′-thiomethyl-2,2′:6′,2″-terpyridine (4′-SMe-T), 4′-methylsulfonyl-2,2′:6′,2″-terpyridine (4′-SO_2-Me-T), 4′-methyl-2,2′:6′,2″-terpyridine (4′-Me-T) and 4′-cyano-2,2′:6′,2″-terpyridine (4′-CN-T) [20,21]. An adaptation of the procedure of Gupton et al. gave 4′-dimethylamino-2,2′:6′,2″-terpyridine (4′-NMe_2-T) [22]. For the synthesis of each [Pt(4′-X-T)Cl]Cl form, the reaction of $Pt(COD)Cl_2$ with the appropriate trpy derivative (4′-X-T ligand) gave the desired product in ~75% yield [23, 24]. The preparation of the counter ion tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) followed the procedure published by Nishida et al. [25]. Finally, the addition of an ethanolic solution of the sodium salt of TFPB to an aqueous solution of the chloride salt of $Pt(4'\text{-X-T})Cl^+$ yielded the desired material [Pt(4′-X-T)Cl]TFPB. Microanalysis and proton NMR data showed that recrystallization from toluene/methylene chloride typically yielded a hemisolvate containing toluene. Microanalysis of [Pt(4′-X-trpy)Cl]TFPB·Y, where Y = toluene; (X = NMe_2·0.5 toluene): *Anal.* Calc.: C, 44.53; H, 2.28; N, 3.956. Found: C, 44.25; H, 2.32; N, 3.73%. (X = CN·0.75 toluene): *Anal.* Calc: C, 45.0; H, 1.98; N, 3.9. Found: C, 44.85; H, 1.98; N, 3.84%. (X = SO_2Me·0.5 toluene): *Anal.* Calc: C, 42.62; H, 1.98; N, 2.89. Found: C, 42.92; H, 2.06; N, 2.88%. (X = SMe): *Anal.* Calc: C, 41.98; H, 1.83; N, 3.06. Found: C, 41.59; H, 1.80; N, 2.90%. The procedure of Hill et al. yielded the $Zn(4'\text{-X-T})Cl_2$ derivatives without need for further purification [26].

A three electrode cell served to obtain the cyclic voltammetry data. In particular, the working electrode was a gold disc, the auxiliary electrode was a Pt wire and the reference electrode was a AgCl/Ag electrode in contact with 3 M NaCl(aq.). For reporting purposes ferrocene served as an internal reference and exhibited a potential of 0.57 V versus AgCl/Ag. The electrolyte solution was 0.1 M TBAH in DMF. This was the solvent of choice because the platinum complexes gave relatively clean waves in this medium, and the zinc complexes showed good solubility. A simple purge with dinitrogen gas sufficed to remove dissolved dioxygen from the sample. The scan rate was usually 50 mV s^{-1}.

For the luminescence studies, a stream of Ar gas acted as the deoxygenating agent. During spectral measurements, the slit settings were 10 nm for both the excitation and emission beams. For emission spectra a 400 nm long-wave-pass filter removed the scattered light, usually at an excitation wavelength of 375 nm. In the case of the lifetime studies the excitation wavelength was either 440 or 420 nm, and the long-wave-pass filter had a cutoff of 475 nm. The laser dye was Coumarin 440 or Stilbene 420, and the solvent for NMR spectra was $CDCl_3$. Dr H. Daniel Lee of Purdue University carried out the microanalyses.

2.3. Instrumentation

The spectrophotometer was a Perkin-Elmer Lambda 4C, and the spectrofluorometer was a SLM-Aminco SPF-500C. For variable temperature measurements the cryostat was an Oxford Instruments model DN1704 system with controller. Descriptions of the procedure and equipment for measuring lifetimes are in the literature [27]. The sweep unit for the electrochemical measurements was a model CV-27 cyclic voltammograph from Bioanalytical Systems.

3. Results

3.1. Electrochemistry

In accord with other platinum(II) complexes of heteroaromatic ligands, the $Pt(4'\text{-X-T})Cl^+$ systems show two ligand reduction waves separated by about 0.6 V in DMF [26,28,29], whereas anodic scans out to the solvent limit gave no indication of platinum oxidation. The potential of the first reduction varies by as much as 0.7 V with the change in the 4′ substituent, whereas the effect on the second reduction is somewhat smaller (Table 1). The second wave is chemically less reversible in that it shows a greater difference in the cathodic and anodic currents. The $Zn(4'\text{-X-T})Cl_2$ analogues also give well-resolved reduction waves that are substituent dependent. In line with the results of Hill et al. who studied the two parent complexes [26], the potential of the

Table 1
Reduction potentials in DMF vs. ferrocene [a]

X	E_1 (V)	E_2 (V)
Zn(4′-X-T)Cl$_2$		
CN	−1.43 (60, 1.0) [b]	
SO$_2$Me	−1.45 (100, 1.4)	
H	−1.86 (70, 1.7)	
SMe	−1.89 (60, 1.4)	
Me	−1.91 (60, 4.0)	
NMe$_2$	−2.12 (70, 1.5)	
Pt(4′-X-T)Cl$^+$		
CN	−0.92 (60, 1.2) [b]	−1.56 (60, 1.4) [b]
SO$_2$Me	−0.98 (60, 1.3)	−1.58 (60, 1.3)
H	−1.24 (70, 1.2)	−1.82 (70, 1.6)
SMe	−1.28 (60, 1.2)	−1.79 (60, 1.5)
Me	−1.30 (70, 1.2)	−1.87 (70, 1.9)
NMe$_2$	−1.53 (70,1.2)	−1.97 (60, 2.5)

[a] From cyclic voltammetry scans at 50 mV s^{-1} in DMF containing 0.1 M TBAH at 23°C.

[b] $E_{pc} - E_{pa}$ (mV), i_c/i_a.

first ligand reduction is ~0.5 V more negative for the zinc complex than it is for the corresponding platinum system.

3.2. Spectroscopy and photophysics

Solutions of the [Pt(4′-X-T)Cl]TFPB compounds are stable in methylene chloride for short periods of time; however, decreases in the near-UV absorption intensity begin to be apparent after 5–6 h. All reported data refer to freshly prepared solutions, except for the low-temperature data where the course of the experiment required ~6 h. As reported previously for the parent trpy complex [9,13], and for the 4′-phenyl-substituted complexes [15], the Pt(4′-X-T)Cl$^+$ systems exhibit one series of intraligand π–π* absorptions centered around 280 nm and another around 320 nm (Fig. 1). Fig. 2 shows that Zn(4′-X-T)Cl$_2$ systems exhibit a similar series of UV absorption bands. Table 2 contains a compilation of absorbance data for the Pt(4′-X-T)Cl$^+$ complexes in two solvents. In addition to the π–π* absorptions, the platinum systems exhibit lesser intensity CT absorption bands in the vicinity of 400 nm. Due to a net reduction of the dipole moment in the CT excited state [13,30], the CT transitions occur at shorter wavelengths in polar solvents like acetonitrile. With the exception of the methyl group, which has almost no effect, the introduction of a substituent in the 4′ position of the trpy ligand induces a bathochromic shift in the CT absorption network (Table 2). This is true whether the substituent group is electron withdrawing or electron donating. As the results in Table 2 show, the presence of the substituent can greatly enhance the intensity of the CT absorption as well. Similar effects are evident in the spectra of 4′-phenyl-substituted Pt(trpy)Cl$^+$ systems [15].

At room temperature, the emission intensity and the lifetime vary dramatically with the nature of the 4′ substituent as well as the solvent. Apart from the 4′-NMe$_2$-T derivative, none of the complexes listed in Table 2 gives a significant emission signal in the room temperature acetonitrile. For the most part, the complexes are emissive in methylene chloride, although the signal is extremely weak for Pt(trpy)Cl$^+$ itself and virtually non-detectable for the closely related 4′-Me-T system. In accordance with the CT absorption data, the introduction of a substituent at the 4′ carbon of the trpy ligand generally causes the emission spectrum to shift to lower energy; however, the emission spectra all appear at rather similar wavelengths. For each system the emission shows well resolved vibrational structure, mono-exponential emis-

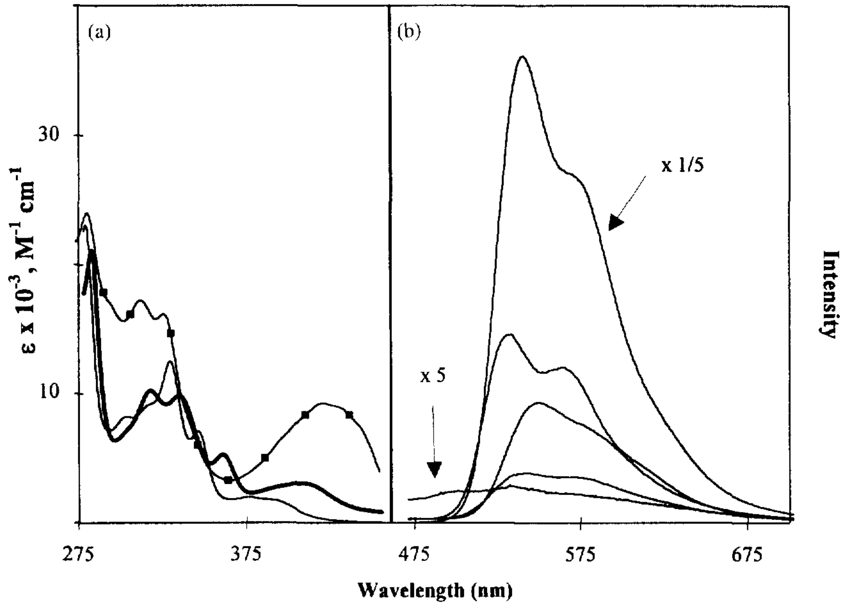

Fig. 1. (a) Near-UV absorption spectra of selected Pt(4′-X-T)Cl$^+$ complexes in MeCN at 23°C: X = NMe$_2$ (–■–), X = CN (-, thick trace), X = H (-, thin trace). (b) Uncorrected emission spectra of Pt(4′-X-T)Cl$^+$ systems in CH$_2$Cl$_2$ at 23°C. The samples all had the same absorbance at the excitation wavelength of 375 nm. In order of increasing intensity at 550 nm the spectra correspond to X = H, SO$_2$Me, CN, SMe and NMe$_2$, respectively.

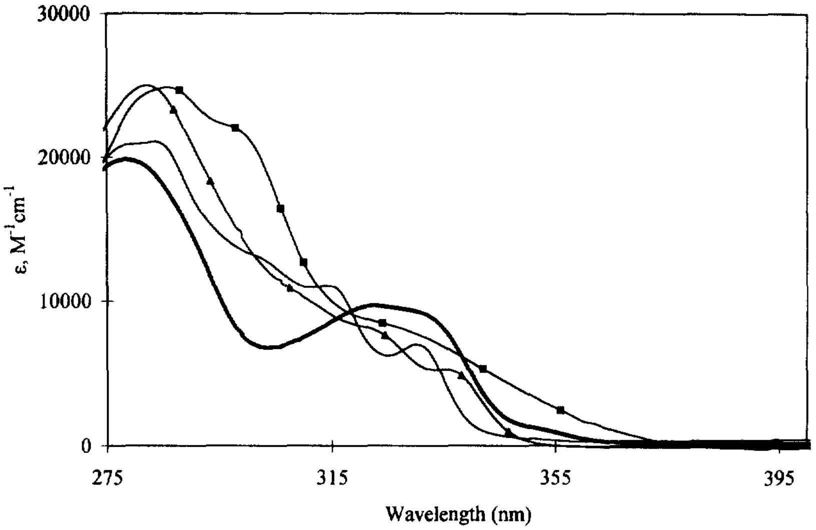

Fig. 2. Near-UV absorption spectra of $Zn(4'\text{-}X\text{-}T)Cl_2$ compounds in DMF at 23°C. The samples have $X = NMe_2$ (– ■ –), X = SMe (– ▲ –), X = Me (-, thin trace) and X = CN (-, thick trace).

sion decay and an excitation spectrum that matches the absorption spectrum. See Fig. 1(b) for some representative spectra. Except for the 4′-Me-T system, the introduction of an electron-withdrawing group or an electron-donating group at the 4′ position of the trpy ligand enhances the lifetime and the emission quantum yield (Table 2). The most dramatic instance is the $4'\text{-}NMe_2\text{-}T$ derivative which has an emission lifetime in the microsecond regime. In view of the emission lifetimes there is little doubt but that in all cases the emission originates from a state with triplet multiplicity. The presence of the well resolved vibronic structure is quite striking and contrasts with the broad emission attributed to metal-to-ligand ^{3}CT excited states of related platinum(II) terpyridine complexes [13,15]. It is entirely possible that the vibronic structure reflects the fact that the emission emanates from states that have significant intraligand excited-state character, vide infra.

Table 2
Absorption and emission data from $Pt(4'\text{-}X\text{-}T)Cl^+$ systems at 23°C

X	λ_{abs} (nm)		Emission data [a]		
	MeCN	CH_2Cl_2	λ_{max} (nm)	ϕ_{em}	τ (ns)
CN		311sh			
	316	323	550	0.005	116
	335	345	590sh		
	(13 800) [b]				
	361	366			
	394	405sh			
	409 (3920)	428			
SO_2Me	316	325	542	0.002	21
	336 (15 200)		577		
	358	348			
	385	380			
	403 (3650)	430			
H	303	305	500	0.0004	< 10
	316	320	535		
	330 (14 200)	340	590		
	346				
	377 (2200)	390			
	390sh	403			
SMe	320	305	542	0.006	142
	333 (17 900)	330	575		
	388	400	625sh		
	409 (7750)	425			
Me	282	284			
	302	308			
	316 (10 100)	322			
	329	336			
	343 (6530)	352			
	374	386			
	390 (2240)	404			
NMe_2	280	282	535	0.08	1920
	311 (17 000)	316	570		
	324 (16 000)	346sh	635sh		
	340sh	420			
	419 (9290)	444			

[a] Emission measurements in CH_2Cl_2.
[b] Molar absorptivity (M^{-1} cm^{-1}).

Temperature-dependent lifetime measurements were only possible over a limited temperature range since methylene chloride is a non-glassing medium. The lack of long-term sample stability was another complication. The complexes selected for detailed studies were $Pt(4'\text{-}SMe\text{-}T)Cl^+$ and $Pt(4'\text{-}CN\text{-}T)Cl^+$. For each complex the data satisfies the following phenomenological equation for the temperature dependence of the lifetime:

$$1/\tau = k_0 + A\exp[-\Delta E/(RT)] \tag{1}$$

The best fit of the data for the 4′-SMe-T complex has a limiting lifetime (k_0^{-1}) of 2.5 μs, a frequency factor (A) of 1.3×10^{10} s^{-1} and an apparent activation energy (ΔE) of 1640 cm^{-1}. The corresponding parameters for the 4′-CN-T complex are 0.25 μs, 1.8×10^{8} s^{-1} and 730 cm^{-1}.

4. Discussion

The goals of this investigation have been to understand the electronic structure of the platinum(II) terpyridine complexes and to develop systems with longer excited state lifetimes. The parent complex Pt(trpy)Cl$^+$ shows no significant photoluminescence intensity in room temperature acetonitrile, although the mixed-ligand trpy complexes that have thiocyanate or hydroxide in place of the chloride ligand are emissive [13]. The systems selected for the present studies involve modified trpy ligands and are freely soluble with TFPB as the counterion in the non-coordinating medium methylene chloride. Although not the principal focus of this work, the electrochemistry of the complexes is germane to the interpretation of the CT spectra. The most important point to recognize is the strong influence substituents have on the first ligand reduction. Electron-donating substituents like SMe or NMe$_2$ shift the potential in the negative direction, while electron-accepting substituents like CN have the opposite effect.

4.1. *Intramolecular charge transfer*

As noted above, the absorption bands with $\lambda_{max} > 350$ nm and $\epsilon > 1000$ M^{-1} cm^{-1} normally correspond to platinum-to-trpy MLCT transitions and therefore involve a type of ligand reduction [13,30]. These band assignments are consistent with the shifts that occur with a change in solvent polarity or the spectator ligand. Comparisons with the low-temperature emission from systems like Ru(trpy)$_2^{2+}$ also reveal that the lifetime and the Stokes shift are compatible with photoluminescence from a corresponding ^{3}CT state [13,31]. Finally, the population of a metal-to-ligand CT state can account for the pronounced emission quenching that occurs in donor solvents like acetonitrile. Due to the increase in the metal's formal oxidation state and the availability of open coordination sites, solvent-induced exciplex quenching is likely to be a very efficient process for such CT states [32–34].

One problem with the concept of a low energy metal-to-ligand CT excited state is the absence of a well defined wave corresponding to the oxidation of the metal center. However, a compensating effect is the fact that the first trpy reduction occurs at an unusually positive potential. Previous investigators have attributed this to a mixing interaction involving the relatively low-lying 6p$_z$ orbital of platinum and an empty π* orbital of the polypyridine ligand [26]. This requires that the redox-active π* orbital (assumed also to be one in the same as the spectroscopically active π* orbital) be antisymmetric with respect to a rotation about the two-fold axis that passes through the ligand. In the notation of Orgel, the symbols ψ and χ designate orbitals that are respectively antisymmetric and symmetric with respect to the two-fold rotation operation [35,36]. Extended Hückel calculations show that the LUMO of the trpy ligand has ψ symmetry [37], and mixing with the higher energy 6p$_z$(Pt) orbital would tend to drive the energy of the corresponding molecular orbital of the complex to even lower energy. The fact that the first ligand reduction is so sensitive to substitution at the 4′ position of trpy is certainly consistent with this interpretation. Thus, mesomeric interactions with donor groups like NMe$_2$ or acceptor groups like CN depend upon overlap with the pπ orbital of the 4′ carbon atom, and this requires an orbital with ψ symmetry. Table 1 reveals that the potential of the second ligand reduction is less sensitive to 4′ substituents. This could mean that the electron enters a ligand orbital with a different symmetry or that this reduction involves a metal-centered orbital [26]. In terms of the spectroscopy, the fact that the introduction of a 4′ CN or SO$_2$Me group induces a bathochromic shift in the CT absorption and emission maxima is easy to appreciate because formation of the excited state at least formally entails a ligand reduction. It is no surprise that an electron-withdrawing group would facilitate the process. However, electron-donating groups like NMe$_2$ and SMe also shift the CT maxima to lower energy, so there are obviously other factors involved. Indeed, a number of recent studies have made the point that CT processes are not just one-electron, center-to-center charge transfers [38,39].

For the platinum(II)–trpy systems at hand, particularly those with electron-donating substituents, the following analysis suggests that a configuration interaction with another CT state has a major influence on the state energies. The literature dealing with substituent effects and the absorption spectrum of benzene illustrate the phenomenon and serve as a useful basis for comparison [40,41]. The important point is that the introduction of either an electron-withdrawing or an electron-releasing substituent induces a red shift in the low energy π–π* absorption of benzene. For example, the lowest energy ^{1}π–π* transition, the so-called α band, occurs around 250 nm in the spectrum of benzene whereas for aniline the corresponding band falls around 285 nm. The reason is clear if one views aniline as a composite molecule containing a benzene ring and a peripheral nitrogen center with an active lone pair [40]. In essence, a configuration interaction with a higher lying nitrogen-to-ring CT state drives down the energy of the π–π* state that is the terminus of the α transition and, at the same time, enhances the oscillator strength. The same kind of effect is evident in the Pt(4′-SMe-T)Cl$^+$ and Pt(4′-NMe$_2$-T)Cl$^+$ systems which exhibit anomalously intense, but relatively low energy CT transitions. Note that the red shifts occur despite the fact that the 4′ substituents are electron donating and destabilize the reduced forms of the respective ligands. The UV spectra of the Zn(4′-X-T)Cl$_2$ analogues

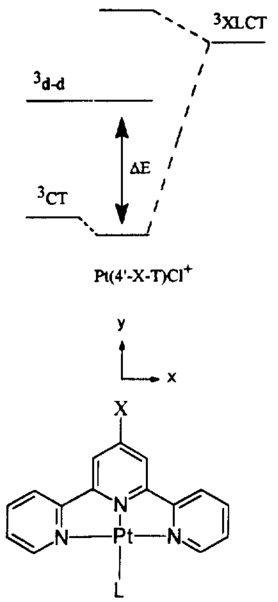

Fig. 3. Axis system and scheme for a configuration interaction between the emitting ^{3}CT state and a ^{3}XLCT intraligand excited state of Pt(4′-X-T)Cl$^+$. The relative energy of the ^{3}d–d state is uncertain, but it may be the thermally accessible state that mediates decay.

are useful for the identification of the participating substituent-to-trpy (XLCT) transitions since there are no interfering MLCT phenomena. Indeed, Fig. 2 shows that, by comparison with Zn(4′-Me-T)Cl$_2$, both the 4′-SMe and the 4′-NMe$_2$ complexes exhibit extra absorption intensity in the region of 290 nm that plausibly reflects XLCT excitation.

The structure given in Fig. 3 is useful for assessing the CT coupling phenomenon. Although the two-fold axis normally defines the z-direction in C_{2v} symmetry, the connections with archetypical D_{4h} complexes are more evident with the proposed choice of axes. However, apart from d(x^2-y^2), the relative order of the d orbitals is unclear in these polypyridine complexes [13,42]. Fortunately, intensity considerations are of some help in making band assignments. According to a simple model, the CT transitions that benefit from the charge-transfer term usually exhibit the bulk of the absorption intensity [43–45], and here these correspond to the y-polarized d(zy) → ψ and d(xz) → χ transitions to ^{1}A$_1$ excited states [13]. In view of the voltammetry data, the transition to the ψ orbital should occur at lower energy. Despite our earlier reservations [13], the CT absorption that occurs in the vicinity of 380 nm for Pt(trpy)Cl$^+$ appears to be intense enough to represent, or include, the d(zy) → ψ transition. For comparison, the reported values of the molar absorptivity of the corresponding visible band of Ru(trpy)$_2^{2+}$, which contains twice as many acceptor ligands, range from 10 000 to 16 000 M^{-1} cm^{-1} [19,31,46]. Thus, the CT absorption intensity is of the same order of magnitude for the platinum system. Since the y-polarized XLCT transition from the lone pair of the NMe$_2$ group also gives rise to a ^{1}A$_1$ excited state, the interaction between the two zero-order ^{1}A$_1$ states produces the state with the absorption maximum at 420 nm in the spectrum of Pt(4′-NMe$_2$-T)Cl$^+$. A simple vector coupling argument based on the collinear transition moments accounts for the increase in the absorption intensity [40]. Exactly the same argument applies to the SMe analogue. By analogy with aniline, there is likely to be further mixing with a π–π* state with ^{1}A$_1$ symmetry. In principle, the same kind of coupling is possible with a ligand-to-metal or a ligand-to-ligand CT state involving the ligand L opposite trpy [1,12]. And when X is electron-withdrawing, coupling to a trpy-to-X state can be important. However, a simple inductive argument is capable of explaining the absorption and the emission data pertaining to the 4′-CN-T and 4′-SO$_2$-T systems, and the absorption spectra of the corresponding Zn(4′-X-T)Cl$_2$ systems do not show any indication of that kind of a CT transition. Nevertheless, the emission from Pt(4′-CN-T)Cl$^+$ occurs at a lower energy than that of the Pt(4′-NMe$_2$-T)Cl$^+$ system. This is not a cause for concern because configuration interaction undoubtedly has a weaker influence on the energy of the triplet state of the 4′-NMe$_2$-T complex. For sure, the dipole–dipole coupling between the two excitations is negligible in the triplet manifold due to the spin forbidden character of each of the CT processes.

4.2. Emission intensities and lifetimes

Contrary to the energy-gap law [47], the unsubstituted trpy complex has the highest energy emission but practically the shortest excited-state lifetime in the whole series. The only system that appears to have a shorter lifetime is the 4′-Me-T complex, and it, too, has a high energy CT absorption. These results are incompatible with direct relaxation from a homologous series of metal-to-ligand CT states [48], but they make sense if another state influences the decay. Suppose that an interaction with another state alters the orbital parentage to differing degrees within the series. Then, the intrinsic lifetimes vary in a way that does not simply depend on the excited state energy. Alternatively, there may be substituent-dependent deactivation through a thermally accessible excited state. The preliminary lifetime-versus-temperature results suggest that both effects are probably important. Although there is clear evidence of thermally activated decay, the nature of the state mediating decay is uncertain. In principle, the state involved could reside within the same potential energy surface. With certain copper(II) and zinc(II) porphyrins, for example, thermal population of vibrationally excited levels of the emitting state fosters decay [49–51]. The same effect can operate in the Pt(4′-X-T)Cl$^+$ systems if the resonance with the intra-ligand excited state alters the shape and/or the equilibrium geometry of the excited-state potential energy surface [52]. Although this mechanism is plausible, the presence of the vibrational structure in the emission spectra suggests that the excited-state surface nests within that of the ground state. If so, vibrationally induced relaxation is unlikely to be of great consequence.

In view of other reports dealing with emissive ^{3}CT states of platinum(II) polypyridines and related systems [13,16,19], it seems more likely that the systems deactivate via a short-lived ^{3}d–d state. The fact that electron-donating substituents could hinder such a pathway is interesting. In the course of their studies of the related $Ru(4'\text{-}X\text{-}T)_2^{2+}$ systems, Maestri et al. have reported that an electron-donating substituent lowers the energy of the first ^{3}d–d state and thereby reduces the barrier to quenching [19]. This makes sense in terms of the orbitals involved. While the lowest unoccupied orbital of the ruthenium system is a dσ^* orbital, the highest occupied orbital is a dπ orbital. The inductive effect of an electron-donating group should destabilize the dσ^* orbital, but the substituent can destabilize the dπ orbital even more because of direct conjugation via the trpy π orbital. With two trpy ligands involved, the upshot is that the deactivating ^{3}d–d state drops to lower energy relative to the ^{3}CT state so that quenching is more efficient. For platinum(II) polypyridines the relative energies of the d orbitals are less certain, but the filled d(z^2) orbital is probably the next highest energy level in these planar systems, in keeping with the importance metal–metal interactions have on packing and the electronic properties [7,8]. Thus, the HOMO and the LUMO of the metal center appear to have dσ^* character so that an electron-donating substituent destabilizes both. If so, the effect on d(x^2-y^2) is likely to be greater due to better overlap with the nitrogen-donor orbitals of the ligand. The upshot would be an increase in the energy of the d–d state as well as ΔE, the activation energy for radiationless decay. However, in view of the uncertain influence that other factors such as configuration interaction with the intraligand excited state have, the diagram in Fig. 3 assumes that the energy of the lowest energy ^{3}d–d state remains essentially constant. Due to the drop in the energy of the emitting CT state, there is still a net increase in the energy required for deactivation via the metal-centered excited state. By the same kind of reasoning, the inductive effect associated with an electron-withdrawing substituent should stabilize the ^{3}d–d state. The effect on the emitting ^{3}CT state is also stabilizing, but even if there is a net increase in ΔE, the effect will not be as dramatic as it is in the case of an electron-donating substituent. The results in Table 2 are obviously in accord with these qualitative predictions based on the assumption of a thermally accessible ^{3}d–d state. On the other hand, the analyses of the temperature-dependent lifetime data yield modest frequency factors. The values obtained are indicative of nested surfaces or perhaps reversible population of the deactivating state [18,53]. Surer identification of the state that mediates the decay will require a great deal more experimental work.

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