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Acid−Base Behavior of the Ground and Excited States of Platinum(II) Complexes of Quinoxaline-2,3-dithiolate

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The acid−base behavior of the ground and excited states of Pt(qdt)$_2^{2-}$ and Pt(phen)(qdt), where qdt = quinoxaline-2,3-dithiolate and phen = 1,10-phenanthroline, has been studied. The pH-dependent changes in the charge-transfer absorption and emission spectra for both complexes are attributed to protonation of the quinoxalinedithiolate ligand at the imine nitrogen. For Pt(qdt)$_2^{2-}$, single protonation leads to a large red shift (2582 cm^{-1}) of the low-energy charge-transfer-to-dithiolate absorption band and the emergence of a new red-shifted emission feature at 728 nm. In solutions of pH below 6, a second protonation takes place at the other qdt ligand, yielding Pt(Hqdt)$_2$. This neutral complex has been isolated and characterized by ^{1}H NMR spectroscopy and elemental analyses. The ground-state basicity constants of the two protonation steps have been determined from spectrophotometric titrations to be pK_{b1} = 6.9 and pK_{b2} = 8.4. Thermodynamic estimation of the excited state pK_{b1}* using a Förster analysis yields values ranging from 1.1 to 1.6, although the apparent pK_{b1}*, obtained by spectrophotometric titration of the emission, is much closer to that of the ground state due to the sub-nanosecond lifetimes of Pt(qdt)$_2^{2-}$ and Pt(Hqdt)(qdt)$^-$ and the kinetics of excited state protonation. For the neutral Pt(phen)(qdt) complex, protonation leads to small changes in the absorption spectrum and quenching of the solution emission. The different protonation behavior between the two complexes results from differences in their electronic structures.

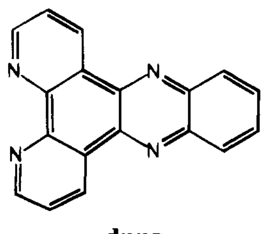
Introduction

Transition metal complexes which are luminescent in solution have been the topic of much investigation because of their potential as photocatalysts for light-to-chemical energy conversion.[1] The photochemical and electron-transfer properties of many systems have been shown to be strongly influenced by the solvent environment, with emission quantum yields, lifetimes, and energies, as well as electron-transfer rates and efficiencies, depending on solvent, ionic strength, and acidity.[2−4]

The effect of solvent pH has been the subject of several reports on the acid−base properties of transition metal chromophores. In 1977, Giordano *et al.* reported on excited state proton transfer involving the carboxylate groups of Ru(bpy)$_2$(dcbpy)$^{2+}$, where bpy = 2,2′-bipyridine and dcbpy = 2,2′-bipyridine-4,4′-dicarboxylic acid.[5] The excited state of this complex is more basic than the ground state due to charge transfer from Ru(II) to the dcbpy ligand. In contrast, the excited state of Ru(bpy)$_2$(dhphen)$^{2+}$, where dhphen = 4,7-dihydroxy-1,10-phenanthroline, was attributed to charge transfer from Ru(II) to a bpy ligand and was found to be more acidic than the ground state.[6] Although the bpy ligand was not directly involved in the deprotonation of Ru(bpy)$_2$(dhphen)$^{2+}$, the depletion of electron density from the metal orbital upon excitation was thought to convey an inductive effect to the dhphen ligand, making it more acidic in the excited state than in the ground state.

Other studies have shown that polyimine ligands in which one or more nitrogen donors remain uncoordinated are protonation sites for emissive Ru complexes and for related systems containing pyrazine, imidazole, or triazole ligands. In each of these cases the predominant emissive state is of the metal-to-ligand charge transfer (MLCT) type with the lowest energy diimine π* orbital as the acceptor. The change in basicity of the complex upon excitation depends on whether the protonation site resides on the chromophoric diimine or one of the ancillary ligands. Protonation of cyanide ligands has also been observed in Ru(LL)$_2$(CN)$_2$,[7] Ru(LL)(CN)$_4$[2,8] and LRe(CO)$_3$CN[9] complexes, and a recent report discusses the changes in emissive properties accompanying protonation of the nitride ligand in *trans*-ReN(Me$_2$PCH$_2$CH$_2$PMe$_2$)Cl$^+$.[10] An excellent review of excited state acid−base behavior has appeared.[11]

Recently, Ru(bpy)$_2$(dppz)$^{2+}$, which contains the bidentate diimine ligand dipyridol[3,2-*a*:2″,3″-*c*]phenazine (dppz), has



dppz

attracted much attention because of its remarkable quenching in aqueous solution relative to the parent Ru(bpy)$_3^{2+}$ chromophore.[12] The complex has been described as a "molecular light switch", and this behavior has led to its use as a probe for

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(1) Balzani, V.; Juris, A. In *Homogeneous and Heterogeneous Photocatalysis*; Pelizzetti, E., Serpone, N., Eds.; D. Reidel Publishing: Dordrecht, Holland, 1985; p 1.

(2) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583−5590.

(3) Sun, H.; Yoshimura, A.; Hoffman, M. Z. *J. Phys. Chem.* **1994**, *98*, 5058−5064.

(4) Prasad, D. R.; Mandal, K.; Hoffman, M. Z. *Coord. Chem. Rev.* **1985**, *64*, 175−190.

(5) Giordano, P. J.; Bock, C. R.; Wrighton, M. S.; Interrante, L. V.; Williams, R. F. X. *J. Am. Chem. Soc.* **1977**, *99*, 3187.

(6) Giordano, P. J.; Bock, C. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 6960−6965.

(7) Davila, J.; Bignozzi, A.; Scandola, F. *J. Phys. Chem.* **1989**, *93*, 1373.

(8) Peterson, S. H.; Demas, N. J. *J. Am. Chem. Soc.* **1979**, *101*, 6571.

(9) Leasure, R. M.; Sacksteder, L. A.; Nesselrodt, D.; Reitz, G. A.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1991**, *30*, 3722−3728.

(10) Vining, W. J.; Neyhart, G. A.; Nielson, S.; Sullivan, B. P. *Inorg. Chem.* **1993**, *32*, 4214.

(11) Vos, J. G. *Polyhedron* **1992**, *11*, 2285−2299.

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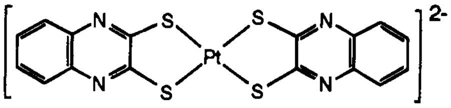
binding to DNA, since the complex is emissive only when the dppz ligand intercalates into DNA, thus protecting it from quenching by water.[13] The mechanism of quenching has been proposed as interaction with water at the nitrogen atoms of the quinoxaline ring, although measurements of ground- and excited-state pK_a values have not been published.

In the present study, we examine the pH-dependent absorption and emission behavior of two Pt(II) quinoxaline-2,3-dithiolate (qdt) complexes, **1** and **2**, that have been found by us previously to be emissive in both low-temperature glasses and ambient-temperature fluid solution. The present study was conducted as a result of observations that showed that, in the presence of acetic acid, solutions of the former complex underwent dramatic color changes.[14] In light of the similarity of the qdt ligand to dppz in having a quinoxaline ring backbone containing imine sites of potential protonation and solvent interaction, an examination of the acid–base behavior of **1** and **2** in their ground and excited states was carried out. Both complexes show evidence for protonation, which results in substantial changes in charge-transfer and emissive properties.



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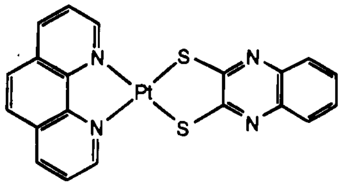

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Experimental Section

Materials, Methods, and Preparations. $(TBA)_2[Pt(qdt)_2]$ and Pt(phen)(qdt) were synthesized as previously described[14] and characterized by ^1H NMR spectroscopy, infrared spectroscopy, and elemental analysis. ^1H NMR spectra were recorded on a Bruker AMX-400 spectrometer operating at 400 MHz. Chemical shifts are reported relative to TMS but were measured on the basis of the internal solvent peak (DMSO-d_6, δ 2.49). Infrared spectra were recorded on a Mattson Galaxy 6020 FTIR spectrophotometer, and samples were prepared as KBr pellets. Absorption spectra were recorded on a Hitachi U2000 UV-visible spectrophotometer. Room-temperature emission measurements were performed on a Spex Fluorolog fluorescence spectrophotometer using a 1 cm × 1 cm quartz fluorescence cell. Room-temperature lifetimes were measured by single-photon counting, as described elsewhere.[15] Solution pH measurements utilized a Fisher Scientific Accumet pH meter with a Corning general purpose combination electrode.

$Pt(Hqdt)_2$. To a methanol solution of 0.010 g of $(TBA)_2[Pt(qdt)_2]$ was added one drop of concentrated HCl. A blue precipitate formed which was separated by centrifugation, washed several times with water to remove (TBA)Cl and excess HCl and then with methanol and ether, and dried under vacuum. IR (KBr, cm^{-1}): 1620 (m), 1506 (w), 1450 (w), 1417 (w), 1380 (m), 1171 (vs), 1139 (vs), 656 (m), 597 (m), 540 (w). ^1H NMR (DMSO-d_6): δ 7.75 (m, 1H), 7.58 (m, 1H). Anal. Calcd for $PtC_{16}H_{10}N_4S_4$: C, 33.04; H, 1.73. Found: C, 32.46; H, 1.94.

Results

(a) pH-Dependent Absorption of $(TBA)_2[Pt(qdt)_2]$. An initial observation upon working with solutions of $(TBA)_2[Pt(qdt)_2]$ was that the bright red color of neutral or basic solutions changed to purple and eventually deep blue when exposed to vapors of acetic acid. The presence of such dramatic color changes in a mildly acidic medium prompted an investigation into the chemical nature of the pH-dependent absorption and a study of the electronic spectra of the qdt complexes as a function of pH. Figure 1 shows the absorption spectrum of $(TBA)_2[Pt(qdt)_2]$ (3.1×10^{-5} M in methanol) and the spectral changes occurring upon addition of 10 μL aliquots of a dilute CH_3COOH solution (4.25×10^{-2} M in methanol). The decrease in the absorbance band at 512 nm is accompanied by the emergence of a new broad feature with a maximum at 590 nm and an increase in absorbance in the 380 nm region. Throughout the titration with acetic acid, clean isosbestic points are maintained at 332, 446, and 566 nm, indicative of the presence of only two absorbing species in solution. The observed spectral changes constitute a red shift of the low-energy feature by 2582 cm^{-1} and will be discussed below in terms of a qualitative molecular orbital picture and estimation of the excited state basicity of the complexes as given by pK_b*. A titration curve, in which the relative change in absorbance at 514 nm is plotted vs the solution pH, is presented in plot a of Figure 2 for a sample of $(TBA)_2[Pt(qdt)_2]$ in aqueous solution with 10% MeOH.

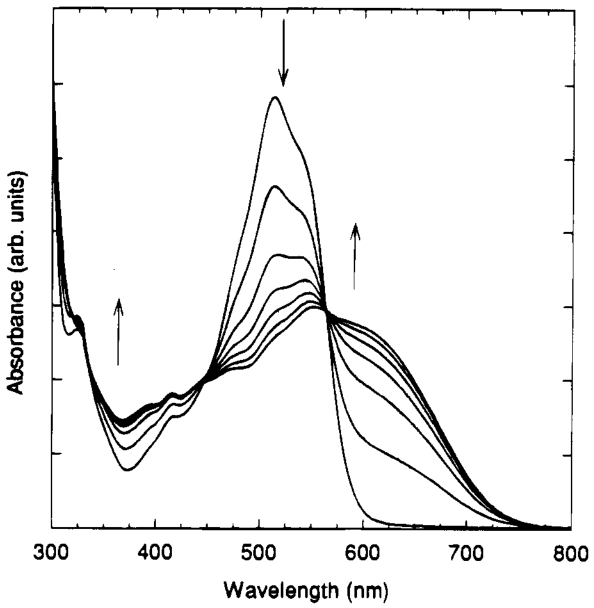

Figure 1. Changes in the absorption spectrum of $(TBA)_2[Pt(qdt)_2]$ (3.1×10^{-5} M) upon addition of 10 μL aliquots of 4.25×10^{-2} M CH_3COOH in methanol.

There are two important observations concerning the absorption spectra which relate to the discussion below on the chemical nature of the pH-dependent absorption. First, the spectral changes described above are fully reversible upon the addition of base such as NaOH, NH_3(aq), or NaOMe. In fact, the isosbestic points listed above are maintained during a back-titration with aliquots of base; there is no difference if acid is added to a basic solution or base is added to an acidic solution. Second, these types of spectral changes are not observed in the absorption spectrum of other, closely related Pt(II) bis(dithiolate) complexes, such as $(TBA)_2[Pt(mnt)_2]$ (mnt = maleonitriledithiolate), upon the addition of acetic acid.

If a strong acid such as HCl is used in place of acetic acid, additional changes are observed in the absorption spectrum beyond those shown in Figure 1. Whereas initially the titration with dilute HCl leads to changes identical to those seen with acetic acid, continued titration leads to loss of the original set of isosbestic points and the emergence of a new set of isosbestic

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(12) Amouyal, E.; Homsi, A.; Chambron, J.-C.; Sauvage, J.-P. *J. Chem. Soc., Dalton Trans.* **1990**, 1841.

(13) Friedman, A. E.; Chambron, J.-C.; Sauvage, J.-P.; Turro, N. J.; Barton, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4960.

(14) Cummings, S. D.; Eisenberg, R. *Inorg. Chem.* **1995**, *34*, 2007–2014.

(15) Zuleta, J. A.; Burberry, M. S.; Eisenberg, R. *Coord. Chem. Rev.* **1990**, *97*, 47–64.

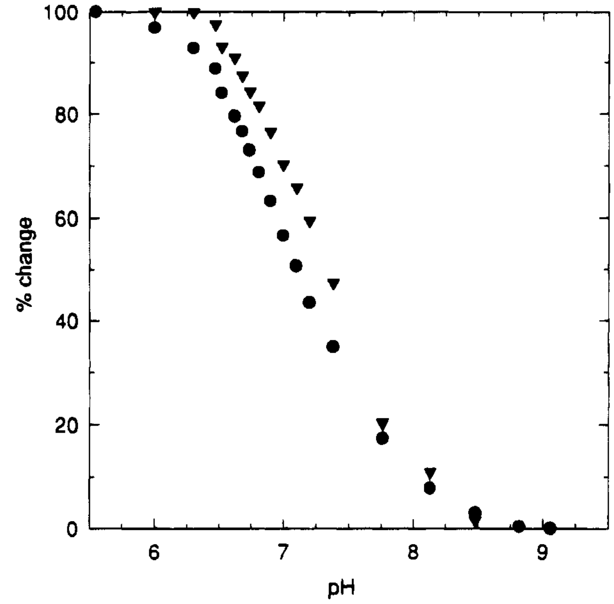

Figure 2. Titration curves for (TBA)$_2$[Pt(qdt)$_2$] in water (10% MeOH added), using (a) percent change in absorbance at 514 nm (●) and (b) percent change in emission intensity at 606 nm (▼) versus pH.

points at 381, 487, and 657 nm. The low-energy band centered at 590 nm resolves into a band with two distinct maxima at 587 and 616 nm, and the absorbance decreases in the 700 and 450 nm regions. These changes are displayed in Figure 3. Qualitatively, the same results are obtained with other acids such as H_2SO_4, HNO_3, or CF_3COOH, and as described above for the titration with CH_3COOH, the process is completely reversible with both sets of isosbestic points maintained sequentially upon neutralization with base.

A blue precipitate forms in the most acidic solutions, especially at higher concentrations of metal complex. This blue product has been characterized as the neutral doubly-protonated Pt(Hqdt)$_2$ complex. Large amounts of this product can be isolated by the addition of one drop of concentrated HCl to a concentrated solution of (TBA)$_2$[Pt(qdt)$_2$] in methanol, followed by washing the resulting blue precipitate repeatedly with water to remove (TBA)Cl. The product has been characterized by ^{1}H NMR spectroscopy and elemental analyses, as described in the Experimental Section. Pt(Hqdt)$_2$ is soluble in DMSO but only slightly soluble in other common solvents. Its ^{1}H NMR spectrum exhibits resonances for the two aromatic protons of the Hqdt ligand, but it does not show a resonance for the N-bound proton.

(b) pH-Dependent Emission of (TBA)$_2$[Pt(qdt)$_2$]. Above pH 8, the emission from (TBA)$_2$[Pt(qdt)$_2$] is independent of solution pH. However, upon addition of acetic acid, the emission band centered at 606 nm loses intensity and a new red-shifted band grows in at 728 nm, having a relative quantum yield for emission, Φ_{em}, approximately 75% that of the (TBA)$_2$[Pt(qdt)$_2$] complex. The observed emission changes are shown in Figure 4 for a 1.1×10^{-4} M solution of (TBA)$_2$[Pt(qdt)$_2$] in methanol with the addition of aliquots of dilute acetic acid. An excitation wavelength of 446 nm coincides with an isosbestic point in the absorption spectrum (Figure 1) in order to ensure a constant sample absorbance during the titration. The maintenance of an isoemissive point at 685 nm indicates that throughout the titration there is a direct conversion from one emitting species to another. In addition, the process is completely reversible, with addition of base regenerating the initial emission profile. The spectra were collected in aerated solutions, but this has been shown previously not to affect the emission energy or quantum yield. Also, the emission quantum yield is not affected by the addition of small amounts of water or by changes in ionic strength that would accompany the addition of acetic acid. Therefore, the spectral changes in the emission are due only to the changing solution pH.

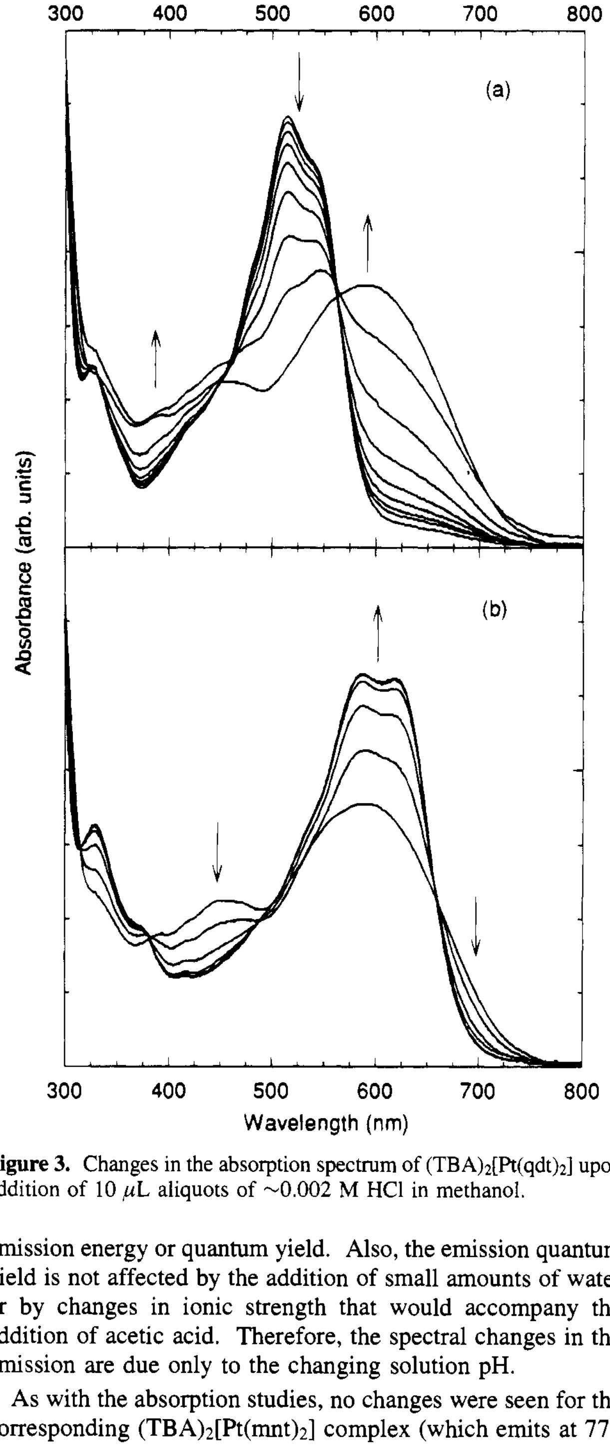

Figure 3. Changes in the absorption spectrum of (TBA)$_2$[Pt(qdt)$_2$] upon addition of 10 μL aliquots of ~0.002 M HCl in methanol.

As with the absorption studies, no changes were seen for the corresponding (TBA)$_2$[Pt(mnt)$_2$] complex (which emits at 775 nm with comparable intensity) under similar conditions and even more acidic conditions.

A titration curve obtained from the relative emission intensity at 600 nm as a function of pH is shown in plot b of Figure 2. The same samples were used in both the absorption and luminescence titration. Emission from the doubly protonated Pt(Hqdt)$_2$ was not observed in solution due to the low solubility in most solvents.

(c) pH-Dependent Absorption for Pt(phen)(qdt). The mixed-ligand complex Pt(phen)(qdt) (**2**) displays changes in its absorption spectrum as solutions are acidified, but the behavior is distinctly different from that of Pt(qdt)$_2^{2-}$. First, spectral changes are not observed when dilute acetic acid is added to solutions of Pt(phen)(qdt) but are seen when HCl is used. Such changes are presented in Figure 5 for a DMF solution of Pt(phen)(qdt) to which aliquots of HCl (3.4 M in DMF) were

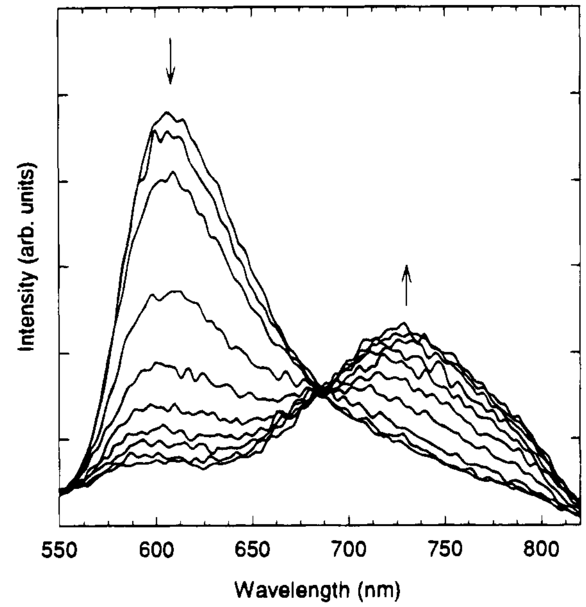

Figure 4. Changes in the emission spectrum of $(TBA)_2[Pt(qdt)_2]$ upon addition of 10 μL aliquots of 4.25 × 10^{-2} M CH_3COOH in methanol.

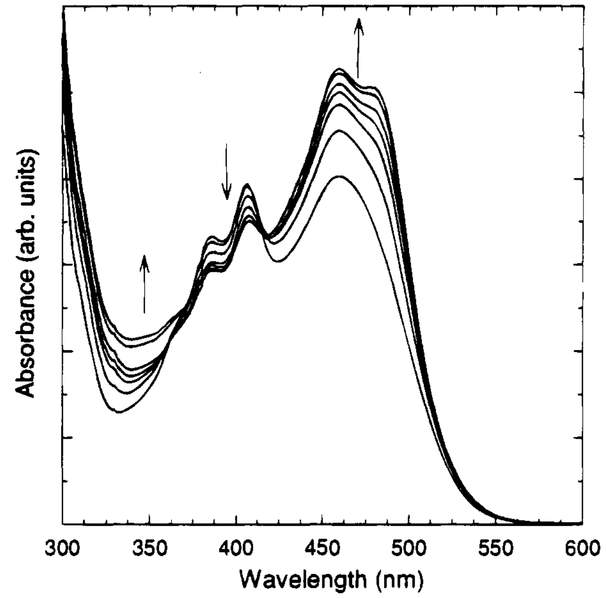

Figure 5. Changes in the absorption spectrum of Pt(phen)(qdt) upon addition of 10 μL aliquots of 3.4 M HCl in DMF.

added. Second, the color changes are much more subtle for this complex compared with the large color changes observed for $Pt(qdt)_2^{2-}$ solutions. In this case, the yellow solution turns slightly orange-brown in solutions of lower pH.

As displayed in Figure 5, during the titration with HCl isosbestic points are observed at 355 and 420 nm, although they are not as clearly defined as for $Pt(qdt)_2^{2-}$. In solutions of low HCl concentration, the same reversibility as was observed for $(TBA)_2[Pt(qdt)_2]$ is found. Namely, the addition of base such as $NH_3(aq)$ to neutralize acidic solutions regenerates the initial spectrum, and during back-titration the same isosbestic points are maintained. Further titration with HCl leads to other spectral changes with a new set of isosbestic points, but the behavior in this lower pH range (pH <4) indicates that the complex may begin to decompose, as the changes are not fully reversible with the addition of base. No such changes in the absorption spectra of other Pt(diimine)(dithiolate) complexes, including Pt(phen)(mnt), were observed upon the addition of HCl. A ground state pK_b of ~9 has been estimated for Pt(phen)(qdt) from the titration of HCl in a DMF solution of the complex.

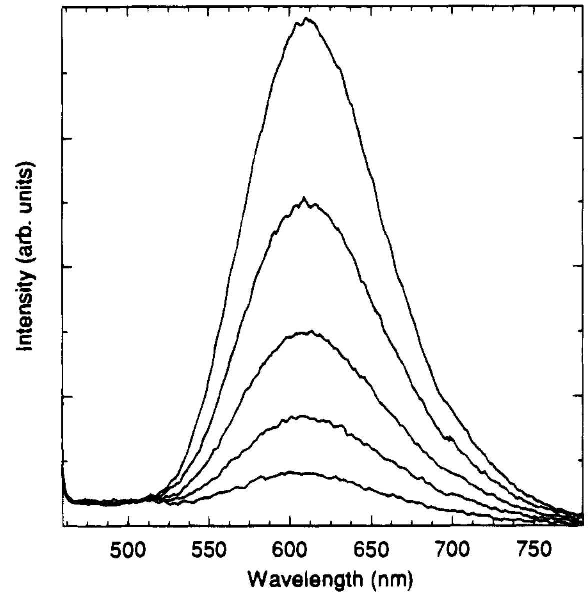

Figure 6. Changes in the emission spectrum of Pt(phen)(qdt) upon addition of 10 μL aliquots of 3.4 M HCl in DMF.

(d) pH-Dependent Emission for Pt(phen)(qdt). The solution luminescence of Pt(phen)(qdt) is quenched in the presence of acid as shown in Figure 6 for the addition of 5 μL aliquots of HCl (3.4 M in DMF) to a solution of Pt(phen)(qdt) (2.6 × 10^{-5} M in DMF). Similar results are seen in other solvents, although the absolute emission intensity is highly solvent-dependent and the amount of acid required depends on the particular solvent choice. Solutions for luminescence titrations were not deoxygenated, and emission quantum yields were determined relative to the unprotonated complex. Samples in undeoxygenated solutions have emission quantum yields 20% smaller than those in deoxygenated solutions. As shown in Figure 6, quenching of the emission by acid in DMF solutions is not accompanied by a shift in the emission maximum or the emergence of any new features. For a titration in acetonitrile a low-intensity emission at ~680 nm is observed at higher HCl concentrations, but it does not increase in intensity when additional HCl is added. For these luminescent titrations, excitation wavelengths corresponding to near-isosbestic points in the absorption spectra were selected to maintain a constant sample absorbance. The solution lifetimes in DMF are listed in Table 1, along with the relative quantum yields for emission, for a series of five solutions of varying HCl concentration. For solutions having a decrease in emission quantum yield corresponding to 58% of the initial value, there is a decrease in lifetime of only 8%.

The changes described for the emission intensity and lifetime of Pt(phen)(qdt) are fully reversible upon neutralization of solutions with base, regenerating the initial emission spectrum and solution lifetime. However, as noted with the results of the absorption data for Pt(phen)(qdt), in solutions with higher HCl concentration, some decomposition may occur, as the emission changes then become only partially reversible. The use of H_2SO_4 yielded the same qualitative results as for HCl, while emission from CH_3CN/H_2O solutions of Pt(phen)(qdt) was found not to be sensitive to the addition of KCl. Finally, solutions of Pt(phen)(mnt) showed no quenching of its 625 nm emission in similar media and HCl concentrations.

Discussion

Both $(TBA)_2[Pt(qdt)_2]$ (**1**) and Pt(phen)(qdt) (**2**) display absorption and emission spectra that are dependent on solution pH. The photophysical and charge-transfer behavior of these complexes has been presented earlier,[14] but a brief description of the significant excited state properties is necessary to discuss the observed acid–base behavior.

The lowest energy excited state of $(TBA)_2[Pt(qdt)_2]$ is a charge-transfer-to-dithiolate state involving electronic excitation from a HOMO which is a mixture of metal and dithiolate orbital character to a LUMO which is a π^* orbital of the dithiolate, a transition which is characteristic of Pt(II) bis(dithiolate) complexes. This transition is observed as a visible absorption band with a maximum at 514 nm (ϵ = 26 100 M^{-1} cm^{-1}) in methanol and a weak emission at 606 nm ($\Phi_{em} = 10^{-5}$). The lifetime of this state in solution is less than 1 ns as estimated from time-correlated spectroscopy.

The complex Pt(phen)(qdt) possesses a distinctly different lowest energy excited state which is termed a charge-transfer-to-diimine state, involving a transition from a HOMO which is a mixture of Pt and dithiolate orbital character to a LUMO which is a π^* orbital of the phenanthroline ligand. Such a transition is characteristic of the mixed-ligand diimine dithiolate system and is observed as a visible absorption which displays a high degree of negative solvatochromism.[16] For Pt(phen)(qdt), this band is found at 465 nm (ϵ = 13 700 M^{-1} cm^{-1}) in DMF. A second higher-energy band which is centered at 395 nm is assigned to a charge-transfer-to-dithiolate transition involving a π^* orbital of the qdt, with orbital contributions similar to that for **1** but shifted to higher energy. Emission from Pt(phen)(qdt) is much stronger in room-temperature solution than for $(TBA)_2[Pt(qdt)_2]$, with an emission maximum at 600 nm which is essentially independent of solvent but a quantum yield for emission which is highly solvent-dependent ($\Phi_{em} = 2.99 \times 10^{-3}$ in $CHCl_3$ and 1.1×10^{-4} in DMSO). Lifetimes are also solvent-dependent and range from 0.117 μs in $CHCl_3$ to 0.030 μs in CH_3CN. This solvent-dependent emission behavior is attributed to increased nonradiative relaxation of the excited state with increased solvent polarity.

The changes which take place in the charge-transfer absorption and emission bands of these complexes at lower solution pH are attributed to either protonation of the chromophore, decomposition of the chromophore, or solvatochromic effects. The weight of the evidence lies in favor of protonation, and several points can be used to argue against the last two effects. The discussion will focus first on $(TBA)_2[Pt(qdt)_2]$, with evidence for protonation of Pt(phen)(qdt) presented later.

Any study of the acid–base properties of a chromophore must rule out decomposition as a cause of spectral changes. For systems studied in highly acidic or alkaline media, this is especially important. In the present case, the changes in absorption and emission are observed in mildly acidic media compared with the majority of other systems described in the literature for transition metal complexes, for which concentrated sulfuric acid solutions are commonly used.[17–19] The dramatic color changes that occur for **1** during acetic acid titration take place between pH 8 and 6. The reversibility of the changes upon neutralization with base and the ability to regenerate the initial spectrum are strong evidence that the complex is not decomposing in acidic solutions. Furthermore, milligram samples of $(TBA)_2[Pt(qdt)_2]$ can be protonated to form the blue product $Pt(Hqdt)_2$ and then can be quantitatively recovered upon addition of NaOH and (TBA)Cl.

Large changes in solution pH constitute a change in the solvent environment which may lead to solvatochromic effects independent of protonations.[20] Several factors rule against this effect in the present case. The solvatochromic shift of the CT absorption band of $(TBA)_2[Pt(qdt)_2]$ with change in solvent polarity is minor when compared with the large spectral changes that accompany acidification. Furthermore, other Pt(II) bis(dithiolate) complexes with similar CT absorption bands display no such changes in acidic media.

Protonation of the $Pt(qdt)_2^{2-}$ chromophore could feasibly take place at a number of different sites, including the metal center, the sulfur atoms, and the nitrogen atoms of the quinoxaline ring. Protonation of the qdt N atoms is supported for two reasons. First, other transition metal qdt complexes have been reported to undergo protonation at the quinoxalinedithiolate N sites, including Ni(II) qdt complexes which have been used as pH indicators[21] and $[Mo(qdt)_3]^{2-}$ which can be protonated three times, once on each ligand.[22] Second, the complex $(TBA)_2[Pt(mnt)_2]$, in which the mnt dithiolate differs from qdt in the absence of the quinoxaline ring backbone, does not undergo protonation under the same conditions or even in more acidic solutions, indicating that protonation of the metal center or sulfur atoms is not a facile process.

In $Pt(qdt)_2^{2-}$, the imine nitrogen of the qdt ligand appears to be a very basic site in the ground state, being protonated in even weakly acidic solutions. Upon protonation of one nitrogen atom, the π^* orbital of the qdt ligand is lowered in energy relative to the unprotonated qdt π^* orbital, which lowers the energy of the CT state of the complex, as well. This is consistent with the observed red shift of the low-energy CT band upon protonation of the complex. In addition, the symmetry of the system is reduced as the two dithiolate ligands become inequivalent, and so a second charge-transfer-to-dithiolate transition involving the unprotonated qdt can be anticipated. Such a band would be expected to lie at slightly higher energy than the CT band of the unprotonated complex since protonation lowers the energy of the Pt orbitals by decreasing the negative charge of the complex and decreasing σ-bonding from the protonated qdt ligand. Indeed, a new absorbance feature is seen to emerge in the 380–480 nm region during the first protonation.

In solutions of lower pH, a second protonation of the chromophore occurs, yielding the neutral $Pt(Hqdt)_2$ complex. This compound has been isolated from acidified solutions of $Pt(qdt)_2^{2-}$ and characterized by ^1H NMR spectroscopy and elemental analyses. We assume that the second protonation occurs at the other qdt ligand rather than at the other imine nitrogen atom of the initially-protonated ligand. The effect on the electronic spectrum of protonating both qdt ligands is to have only one CT band which lies at an energy lower than that for the fully deprotonated complex. This is illustrated in the absorption spectra at lower pH (Figure 3), where the absorbance which had emerged in the 380–480 nm region now decreases and the lowest energy feature resolves to an intensity and band shape similar to those of the CT band of the unprotonated form, but at ~2500 cm^{-1} lower energy.

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(16) Zuleta, J. A.; Bevilacqua, J. M.; Eisenberg, R. *Coord. Chem. Rev.* **1992**, *111*, 237.

(17) Crutchley, R. J.; Kress, N.; Lever, A. B. P. *J. Am. Chem. Soc.* **1983**, *105*, 1170–1178.

(18) Kirsch-De Mesmaeker, A.; Jacquet, L.; Nasielski, J. *Inorg. Chem.* **1988**, *27*, 4451–4458.

(19) Hosek, W.; Tysoe, S. A.; Gafney, H. D.; Baker, A. D.; Strekas, T. C. *Inorg. Chem.* **1989**, *28*, 1228–1231.

(20) Suppan, P. *J. Photochem. Photobiol. A* **1990**, *50*, 293.

(21) Rignedoli, A.; Peyronel, G.; Malavasi, W. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1963–1966.

(22) Boyde, S.; Garner, C. D.; Enemark, J. H.; Ortega, R. B. *J. Chem. Soc., Dalton Trans.* **1987**, 297.

Since there are three forms of the chromophore, namely the unprotonated, singly protonated, and doubly protonated species shown in eq 1, the accuracy in determining the ground state pK_b

$$\mathrm{Pt(qdt)_2}^{2-} \underset{-\mathrm{H}^+}{\overset{+\mathrm{H}^+}{\rightleftharpoons}} \mathrm{Pt(Hqdt)(qdt)}^- \underset{-\mathrm{H}^+}{\overset{+\mathrm{H}^+}{\rightleftharpoons}} \mathrm{Pt(Hqdt)_2} \qquad (1)$$

values will depend on how well separated the pK_b values associated with these two equilibria are. For many of the transition metal systems in which multiple protonations occur, the resolution of the individual steps is poor and is marked by an absence of distinct isosbestic points in the absorption spectra.[19,23] In the present case, however, the two protonation steps can be separated conveniently by the appropriate choice of acid titrant, as only the singly protonated species forms in dilute acetic acid/methanol solutions. During the titration with CH_3COOH, a set of clean isosbestic points is maintained throughout the conversion from the unprotonated dianionic complex to the singly-protonated species. Therefore, the data in Figure 2 can be used to calculate the ground-state pK_{b1} from the inflection point of the titration curve. A value of pK_{b1} = 6.9 supports the notion that this complex is moderately basic, with its first pK_b significantly larger than the pK_b for both quinoxaline (13.64) and pyrazine (13.35) and closer to those of pyridine (8.75) and 2-aminopyridine (7.18).[24] However, the complex is less basic than the uncoordinated sodium salt of quinoxaline-2,3-dithiol (pK_{b1} = 4.05, pK_{b2} = 7.16), which upon protonation is in the dithioamide form rather than the quinoxalinedithiol form since the nitrogen sites are more basic than the sulfur atoms.[25] Reduction of the basicity upon coordination of the dianionic ligand to the Pt(II) ion is consistent with the strong σ-donating ability of the sulfur atoms and is similar to the reduced basicity of most diimines in Ru polypyridyl complexes with ligand-based sites of protonation.[11]

Data from the titration with HCl were used to obtain an estimate of the basicity constant of the second protonation step, pK_{b2}, using the same analysis. The second protonation occurs at a pH significantly lower than that required for the first protonation so that the two pK_b values are well separated. From the inflection point of the titration curve, a pK_{b2} of 8.4 was determined. The imine nitrogen of the second qdt ligand thus has a pK_b value close to that of pyridine.

Changes in the emission spectrum of $\mathrm{Pt(qdt)_2}^{2-}$ upon titration with acetic acid are shown in Figure 4 and are proposed to be a result of the first protonation described above. Upon protonation, the CT emission band at 606 nm is red-shifted 2765 cm^{-1} to a broad, featureless band centered at 728 nm which has comparable intensity. The smooth conversion displayed during the titration and the maintenance of an isoemissive point indicate that there are only two emitting species in solution. The band at 728 nm is therefore assigned to emission from $\mathrm{Pt(qdt)(Hqdt)}^-$.

The emission from $\mathrm{Pt(qdt)(Hqdt)}^-$ relative to that from $\mathrm{Pt(qdt)_2}^{2-}$ stands in contrast to the situation for the majority of other transition metal chromophores for which protonation of ligand-based imine nitrogen sites has been studied. In those cases, the solution emission is usually quenched at lower pH, although for some cases very weak emission is attributed to the protonated complex. In this case, both the protonated and unprotonated forms are emissive, albeit with low emission quantum yields. Attempts to determine the excited state lifetimes of $\mathrm{Pt(qdt)_2}^{2-}$ and $\mathrm{Pt(Hqdt)(qdt)}^-$ yielded upper limits of 1 ns in room-temperature solutions.

The observed red shift of the emission upon protonation is consistent with an assignment of a charge-transfer-to-dithiolate emitting state. As with the absorption, protonation of the qdt imine nitrogen lowers the energy of the π^*(qdt) LUMO while having little effect on the metal-based HOMO, thereby lowering the energy of emission. Although the emitting state may be of multiplicity different from that of the absorbing state, this should not change the qualitative differences in energy between the orbitals on the protonated and unprotonated forms of the complex.

Excitation to a charge-transfer-to-dithiolate state should make $\mathrm{Pt(qdt)_2}^{2-}$ a stronger base in the excited state, since there is a net increase in electron density in the qdt ring relative to the ground state. Furthermore, protonation of the complex should stabilize the more basic excited state to a greater extent than the less basic ground state. The large red shifts observed in both the charge-transfer absorption and emission bands upon protonation are consistent with a more basic excited state. The excited-state basicity constant, pK_b*, should therefore be smaller than the ground-state constant pK_b.

An estimate of pK_b* values can be achieved using a simple relationship developed by Förster and employed with varying success for many acid–base systems. Based on purely thermodynamic principles, Förster's analysis yields an equation which relates pK_b* to pK_b using only the frequencies of the E_{0-0} transition for the basic (ν_B) and protonated (ν_{BH^+}) forms of the complex:

$$\mathrm{p}K_b^* = \mathrm{p}K_b - \frac{Nh}{2.303RT}(\nu_B - \nu_{BH^+}) \qquad (2)$$

where N is Avogadro's number, h is Planck's constant, R is the gas constant, and T is the temperature. The use of this equation requires two approximations to be made. First, the entropies of ground- and excited-state protonations are assumed to be equal. Second, the frequencies of the E_{0-0} transitions for the acid and base forms of the complex must be estimated in the absence of highly structured absorption or emission profiles. For transition metal complexes with triplet excited states, emission energies should provide a more accurate estimation of the E_{0-0} transition frequencies, although some researchers have found more satisfactory results when using absorbance maxima.[23] The use of emission maxima for $\mathrm{Pt(qdt)_2}^{2-}$ (606 nm) and $\mathrm{Pt(Hqdt)(qdt)}^-$ (728 nm) yields a ΔpK_b of 5.8 and an excited-state pK_b* of 1.1. If absorption maxima are used instead, a ΔpK_b of 5.3 and an excited-state pK_b* of 1.6 are calculated. Qualitatively, these results indicate that the Förster analysis predicts an excited state which is significantly more basic than the ground state.

The Förster analysis of pK_b* for eq 1 takes only the thermodynamics of the excited states into account, ignoring important kinetic factors. The analysis assumes that equilibrium is achieved in the excited-state proton-transfer reactions. However, for acid–base conjugate complexes with short-lived excited states such as $\mathrm{Pt(qdt)_2}^{2-}$ and $\mathrm{Pt(Hqdt)(qdt)}^-$, the acid–base equilibrium of the excited state may never be reached kinetically. An illustration of the relevant species is given in Scheme 1, where k_1, k_{-1}, k_1*, and k_{-1}* are the rate constants for protonation and deprotonation, respectively, of the ground and excited states and k_r, k_{nr}, k_r', and k_{nr}' are the radiative and nonradiative rate constants for the unprotonated and protonated excited-state species. With emission quantum yields of only 10^{-5} and lifetimes less than 1 ns in solution for $\mathrm{Pt(qdt)_2}^{2-}$ and

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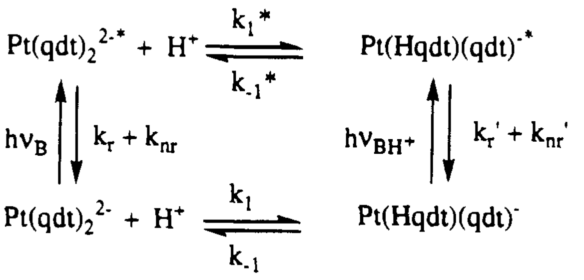
(23) Nazeeruddin, M. K.; Kalyanasundaram, K. *Inorg. Chem.* **1989**, *28*, 4251–4259.

(24) *CRC Handbook of Chemistry and Physics*, 66th ed.; CRC Press: Boca Raton, FL, 1986; pp D159–D160.

(25) Dalziel, J. A. W.; Slawinski, A. K. *Talanta* **1972**, *19*, 1240.

Scheme 1



$Pt(Hqdt)(qdt)^-$, the rates of deactivation of the excited states, $k_r + k_{nr}$ and $k_r' + k_{nr}'$, are probably much faster than the proton-transfer rates k_1* and k_{-1}*. The emission titration curve (Figure 2) demonstrates the importance of kinetic factors in excited-state proton-transfer reactions, yielding an "observed" pK_b* of 6.7, which is nearly the same as the ground-state pK_b of 6.9.

The neutral complex Pt(phen)(qdt) possesses excited-state properties very different from those of $Pt(qdt)_2^{2-}$, and so it was expected that this complex would display different acid–base properties as well. As described under Results, these differences are observed in both the absorption and emission spectra.

The spectral changes for solutions of Pt(phen)(qdt) upon the addition of strong acid are proposed to be the result of protonation of the qdt imine N atom rather than either a solvatochromic shift due to changes in solvent polarity or decomposition of the metal complex on the basis of several observations. First, protonation of the qdt N appears to be facile for $Pt(qdt)_2^{2-}$ and other transition metal qdt complexes and so would be expected to occur for Pt(phen)(qdt) at an appropriate pH as well. Second, protonation at other sites of the complex, such as at the metal center or the phenanthroline ring, are rejected by the lack of precedents and by the observation that the complex Pt(phen)(mnt), which differs from Pt(phen)(qdt) only in the absence of a quinoxaline backbone in an otherwise electronically similar dithiolate ligand, undergoes no such spectral changes at low pH. Third, while solvatochromic effects are large for the low-energy band of this complex, they lead to changes qualitatively different from those shown in Figure 5. Specifically, solvatochromic shifts only occur for the CT band which is found between 425 and 600 nm, with no changes occurring in the 300–425 nm region. Finally, in solutions having a pH above 4, the complex appears to be stable with spectral changes that are fully reversible, although for solutions below this pH decomposition may occur. Graphical analysis and isosbestic points indicate only two species exist in solution in this pH range, corresponding to the equilibrium shown as eq 3.

$$\mathrm{Pt(phen)(qdt)} \overset{\mathrm{H}^+}{\rightleftharpoons} \mathrm{Pt(phen)(Hqdt)}^+ \qquad (3)$$

Protonation of Pt(phen)(qdt) differs from the protonation of $Pt(qdt)_2^{2-}$ in three respects: the larger pK_b value, the smaller degree of spectral changes in the absorption spectrum, and the quenching of emission intensity, each of which can be understood in terms of the differences in electronic structure between the two metal complexes. First, the larger pK_b of Pt(phen)(qdt) (pK_b ~ 9) relative to $Pt(qdt)_2^{2-}$ (pK_b = 6.9) reflects the decreased basicity of the N site of the qdt ligand in the former complex. This is almost certainly a result of the neutral charge of Pt(phen)(qdt) compared to the dianionic charge of $Pt(qdt)_2^{2-}$.

The changes observed in the absorption spectrum upon protonation (Figure 5) do not include any new feature emerging at lower energy, as was observed for complex **1**, which reflects the differences in the charge-transfer absorption bands of the two complexes. Protonation of the qdt ligand of **2** will influence the energies of the two charge-transfer absorption bands that involve orbital contributions from the dithiolate. The charge-transfer-to-dithiolate band centered at 395 nm, which is assigned to a charge transfer to a qdt π* LUMO, will be affected by protonation in a manner similar to that described for complex **1**, resulting in a red shift of the higher-energy band. This shift, however, appears to be obscured by the lower energy charge-transfer-to-diimine band at 465 nm. The 465 nm transition involves a HOMO localized on the dithiolate and metal center and a LUMO localized on the phenanthroline ligand, as supported by spectroscopic studies[14] and molecular orbital calculations.[26] Since the π* dithiolate orbital is not involved directly in this transition, protonation of the qdt ligand is expected to lead to only a small degree of stabilization of the energy of the HOMO, while the energy of the phenanthroline π* LUMO remains unchanged. The result is a modest blue shift in the lowest energy CT band. These two contrary spectral shifts obscure each other, but the net effect is consistent with the small changes observed in the intensity and energy of the features in the 300–550 nm region of the absorption spectrum of Pt(phen)(qdt).

Table 1. Relative Emission Quantum Yields (Φ_{rel}) and Excited-State Lifetimes (τ) for Pt(phen)(qdt) in DMF upon Addition of HCl

Φ_{rel}	[HCl] (M)	τ (ns)
1.00	0	32.9
0.87	9×10^{-4}	32.5
0.81	5.9×10^{-3}	32.0
0.66	1.20×10^{-2}	30.4

The observed changes in emission quantum yield upon addition of HCl also arise from the protonation of the qdt imine nitrogen site. This conclusion is supported by the facts that (1) the changes that occur in the luminescence coincide with the changes in absorption, (2) the changes are fully reversible upon neutralization, regenerating the unprotonated complex, and (3) no similar changes are observed for Pt(phen)(mnt), which is not protonated.

In contrast to the case of $Pt(qdt)_2^{2-}$, emission from Pt(phen)(qdt) is quenched using strong acids in DMF solution without the observation of emission from the protonated complex. We have previously reported the effects of solvent on the emission quantum yield and lifetime of Pt(phen)(qdt).[14] Nonradiative rate constants increase in solvents of increasing polarity, resulting in a decreased quantum yield and shortened lifetime. The quenching of the emission quantum yield using strong acids is not accompanied by a significant decrease in the excited-state lifetime (see Table 1), indicating that it occurs by a mechanism that does not involve a change in either the radiative or nonradiative decay rate constants. Strong acids such as HCl are not capable of energy- or electron-transfer quenching, and deactivation by Cl^- has also been ruled out because the addition of KCl leads to no changes in the luminescence. The observed changes are therefore due to a *static* quenching effect, and the protonated form of the complex is nonemissive.

This result may be contrasted with different effects that involve ligand protonation in Ru(II) polypyridyl systems. For example, quenching of the MLCT emission of $Ru(bipyrazine)_3^{2+}$ occurs by a dynamic mechanism that follows Stern–Volmer kinetics, and excited-state protonation leads to a decrease in emission intensity as well as a decrease in excited-state lifetime.[11] The work of Long and Vos demonstrated that protonation of the imine nitrogen atoms in $Ru(bpy)_2(imidazole)_2^{2+}$ and $Ru(bpy)_2(1,2,4\text{-triazole})_2^{2+}$ complexes leads to a large

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(26) Cummings, S. D.; Eisenberg, R. Unpublished results.

increase in the luminescence quantum yield.[27] These results suggest that the excited-state dynamics of conjugate acid–base chromophores may be influenced by a variety of different factors, including vibronic relaxation and electronic effects.

The lack of observed emission from the protonated form of complex **2** is consistent with an electronic structure in which the emissive charge-transfer-to-diimine state has been raised in energy above a nonemissive state, possibly the charge-transfer-to-dithiolate state or a metal-centered d–d state. Effects very similar to this have been observed for the Ru(diimine)$_2$(CN)$_2$ and Re(diimine)(CO)$_3$CN systems, for which protonation of the CN ligand led to a raising of the d(Re)–π^*(diimine) MLCT state above the π–π^*(diimine) state, as observed by changes in the emission energy and structure.

Conclusions

The complexes (TBA)$_2$[Pt(qdt)$_2$] and Pt(phen)(qdt) can be protonated by acids at the imine nitrogen of the qdt ligand. Protonation has the largest effect on charge-transfer excited states which involve the qdt ligand. For (TBA)$_2$[Pt(qdt)$_2$], the lowest-energy excited state involves charge transfer into a qdt π^* orbital. A large red shift of the CT absorption and emission band energies is observed, which is consistent with stabilization of the qdt π^* orbital upon protonation. For Pt(phen)(qdt), the lowest-energy excited state involves charge transfer from an orbital of mainly Pt(d)/S(p) character to a phen π^* orbital. The ^{3}CT emission observed for Pt(phen)(qdt) is not observed upon protonation of the complex. It is proposed that the absence of emission results from a change in the nature of the lowest excited state upon protonation.

The large changes in the charge-transfer absorption and emission which accompany protonation of (TBA)$_2$[Pt(qdt)$_2$] and the relatively mild pH conditions at which they occur are unique aspects of this work. The ease with which the complex is protonated relative to most other transition metal lumophores is a reflection of its dianionic charge. Relatively few transition metal lumophores are anionic, compared with an abundance of cationic or neutral complexes. However, the solution luminescence for this complex is weak and lifetime of the excited state is very short. The development of new anionic complexes which possess long-lived excited states and have basic sites may be of interest in developing photocatalysts for proton reduction. Chromophores which are easily protonated and have increased basicity upon excitation would be ideal for studies of this nature.

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[27] Long, C.; Vos, J. G. *Inorg. Chim. Acta* **1984**, *89*, 125–131.