

## Luminescent Platinum(II) Complexes of Quinoxaline-2,3-dithiolate

Scott D. Cummings and Richard Eisenberg\*

Department of Chemistry, University of Rochester, Rochester, New York 14627

Received July 15, 1994<sup>®</sup>

The synthesis, characterization, and photophysical properties of several Pt(II) complexes of quinoxaline-2,3-dithiolate (qdt) and 6,7-dimethylquinoxaline-2,3-dithiolate (dmqdt) are described. Specifically,  $(\text{TBA})_2[\text{Pt}(\text{qdt})_2]$ , where TBA = tetra-*n*-butylammonium,  $\text{Pt}(\text{COD})(\text{qdt})$ , where COD = 1,5-cyclooctadiene, and  $\text{Pt}(\text{phen})(\text{qdt})$ , where phen = 1,10-phenanthroline, and their dmqdt analogs have been prepared and examined with respect to their photophysical properties. Highly structured emission from  $\text{Pt}(\text{COD})(\text{qdt})$  in frozen glass solution at 77 K has been detected, having a major vibrational progression of  $1370\text{ cm}^{-1}$  corresponding to a C=C stretching frequency of the quinoxalinedithiolate backbone. Solution luminescence from  $(\text{TBA})_2[\text{Pt}(\text{qdt})_2]$  and  $\text{Pt}(\text{phen})(\text{qdt})$  has been detected with quantum yields,  $\Phi_{\text{em}}$ , of  $10^{-5}$  and  $10^{-3}$ , respectively, although the latter is highly sensitive to solvent effects. The complex  $\text{Pt}(\text{phen})(\text{qdt})$  possesses a low-energy ( $\lambda_{\text{max}} = 497\text{ nm}$  in  $\text{CHCl}_3$ ) absorption band assigned to a charge-transfer-to-diimine transition which exhibits a high degree of negative solvatochromism. Through both emission quantum yield and excited state lifetime measurements, the emissive excited state of  $\text{Pt}(\text{phen})(\text{qdt})$  is shown to undergo increasing degrees of nonradiative deactivation with increasing solvent polarity. Reductive quenching of the excited state of  $\text{Pt}(\text{phen})(\text{qdt})$  has been examined using the aromatic amines *N,N*-dimethylaniline (DMA) and *N,N,N',N'*-tetramethylphenylenediamine (TMPD). From a Stern–Volmer analysis of the emission quenching data, quenching rate constants of  $2.8 \times 10^9\text{ s}^{-1}$  (DMA) and  $6.9 \times 10^9\text{ s}^{-1}$  (TMPD) were calculated. Cyclic voltammetry was conducted on each of the complexes in order to probe further the nature of the HOMO and LUMO. From a simple thermochemical analysis, an excited state reduction potential of 1.14 V (vs NHE) has been estimated for  $\text{Pt}(\text{phen})(\text{qdt})$ .

## Introduction

Emission from square-planar Pt(II) systems has been known for decades, with early studies focusing on the luminescence of solid samples of tetracyanoplatinate and tetrahaloplatinate salts at low temperatures.<sup>1</sup> In recent years, there has been a growing interest in the excited state properties of new Pt(II) complexes, driven by the discovery that some of these systems possess long-lived excited states and luminesce in fluid solution at ambient conditions, properties which indicate potential uses for photocatalysis. The development of photocatalysts for light-to-chemical energy conversion depends on understanding what factors influence the thermodynamic and kinetic parameters of the excited state complexes.

Most of the information regarding the excited states of Pt(II) complexes has been obtained from studies of luminescence from both solid state and solution samples. A variety of excited states have been characterized by these studies, with the lowest-energy excited state in a complex depending on the ligands coordinated to the Pt(II) ion. Although emission from metal-centered (MC) d–d states is rare due to efficient radiationless deactivation, low-temperature luminescence from  $\text{PtX}_4^{2-}$  (X = halide) systems has been attributed to MC excited states. Metal complexes containing ligands with  $\pi$  systems may possess intraligand (IL)  $\pi$ – $\pi^*$  states and metal-to-ligand charge transfer (MLCT) d– $\pi^*$  states or states which are mixtures of these two limiting cases. For example, low temperature emission from  $\text{Pt}(\text{8-quinolinol})_2$  has been assigned to a  $^3\text{IL}$  state which is “metal-perturbed”, and emission from a series of  $[\text{Pt}(\text{terpyridine})\text{X}]^{n+}$  complexes has been assigned to  $^3\text{MLCT}$  excited states for X = halide,  $\text{N}_3^-$ , and  $\text{SCN}^-$  and  $n = 1$ , but for X =  $\text{NH}_3$  and  $n = 2$  the state has more  $^3\text{IL}$  character.<sup>2</sup> In some cases, small changes in the ligands lead to distinct differences in the photoluminescent behavior. The  $^3\text{MLCT}$  emission from cyclo-

metalated complexes  $\text{Pt}(\text{2-phenylpyridine})_2$  and  $\text{Pt}(\text{benzoquinoline})_2$  is detectable only at low temperature, while the corresponding  $\text{Pt}(\text{thienylpyridine})_2$  complex is luminescent in solution at room temperature.<sup>3</sup> Similar tuning of emissive properties has been reported for  $\text{Pt}(\text{pQP})^{2+}$ , where pQP = 3'',5,5',5'''-tetramethyl-2,2':6',2'':6'',2'''-quaterpyridine, which displays bright, long-lived solution emission although the corresponding unethylated quaterpyridine complex does not.<sup>4</sup>

Other types of excited states have been characterized which arise from interaction of two or more square-planar Pt(II) complexes. The stacking of  $\text{Pt}(\alpha\text{-diimine})\text{Cl}_2$  and  $\text{Pt}(\alpha\text{-diimine})_2^{2+}$  in the solid state led to new emission features which were attributed to  $\pi$ – $\pi$  interactions of the diimine ligands.<sup>5</sup> However, for  $\text{Pt}(\alpha\text{-diimine})(\text{CN})_2$  complexes, the emission was proposed to originate from a state involving Pt  $d_{z^2}$  and diimine  $\pi^*$  orbitals.<sup>6</sup> In addition, excimer emission has been detected from concentrated solutions of  $\text{Pt}(\text{4,7-diphenyl-1,10-phenanthroline})(\text{CN})_2$ .<sup>7</sup> Finally, the binuclear  $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$  complex possesses a long-lived excited state which involves a metal–metal bonding interaction and has displayed some fascinating excited state chemical reactivity, including proton reduction to  $\text{H}_2$  and H atom abstraction from alkanes.<sup>8</sup>

Our laboratory has focused on the photochemical properties of Pt(II) dithiolate complexes. For the series  $\text{Pt}(\text{COD})(\text{SS})$  and  $\text{Pt}(\text{LL})(\text{SS})$ , where COD = 1,5-cyclooctadiene, LL = chelating diphosphine or monodentate phosphines and phosphites, and SS = dithiolate, these complexes display low-temperature emission arising from a MLCT excited state which involves a

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, March 15, 1995.

(1) Lechner, A.; Glieman, G. *J. Am. Chem. Soc.* **1989**, *111*, 7649.  
 (2) Yip, H.-K.; Cheng, L.-K.; Cheung, K.-K.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1993**, 2933.

(3) Maestri, M.; Sandrini, D.; Balzani, V.; Chassot, L.; Joliet, P.; von Zelewsky, A. *Chem. Phys. Lett.* **1985**, *122*, 375.

(4) Chan, C.-W.; Che, C.-M.; Cheng, M.-C.; Wang, Y. *Inorg. Chem.* **1992**, *31*, 4874–4878.

(5) Miskowski, V. M.; Houlding, V. H. *Inorg. Chem.* **1989**, *28*, 1529–1533.

(6) Che, C.-M.; He, L.-Y.; Poon, C.-K.; Mak, T. C. W. *Inorg. Chem.* **1989**, *28*, 3081–3083.

(7) Kunkely, H.; Vogler, A. *J. Am. Chem. Soc.* **1990**, *112*, 5625–5627.

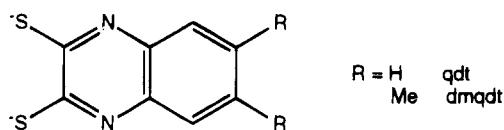
(8) Zipp, A. P. *Coord. Chem. Rev.* **1988**, *84*, 47–83.

$\pi^*$  orbital of the dithiolate.<sup>9,10</sup> For complexes in which LL =  $\alpha,\alpha'$ -diimine, room-temperature luminescence in fluid solution and highly solvatochromic charge-transfer absorptions are seen, arising from an excited state which involves a  $\pi^*$  orbital of the diimine.<sup>11</sup> In addition to the different photophysical properties associated with changing the nature of the LL donor ligands, the dithiolate plays a key role in determining the excited state behavior of these complexes. Distinct differences between Pt(II) complexes of maleonitriledithiolate (mnt) and 1-(ethylcar-

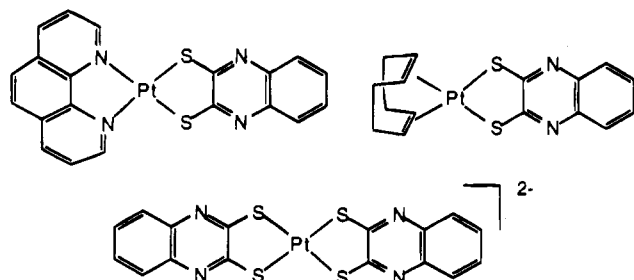


boxy)-1-cyanoethylene-2,2-dithiolate (ecda) have been observed. Specifically, complexes of the 1,2-dithiolate mnt display vibrationally structured emission having single-exponential decay, while complexes of the 1,1-dithiolate ecda possess unstructured emission having multiexponential decay. Most of the previous work has been limited to complexes of these two dithiolate ligands.

To better understand how changes in the nature of the dithiolate can alter the photochemical properties of the metal-dithiolate chromophore, we have undertaken an investigation of related Pt(II) complexes having other dithiolate ligands. The present study focuses on the luminescent properties of Pt(II) complexes containing quinoxaline-2,3-dithiolate (qdt) or its



dimethyl derivative. Many reports on homoleptic metal complexes of qdt have appeared in the literature, primarily concerning the use of qdt as an analytical chelating agent<sup>12</sup> and utilization of qdt complexes as ion-active substances of membrane electrodes.<sup>13</sup> Recently Mo(qdt)<sub>2</sub><sup>3-</sup> was investigated for modeling of molybdenum hydroxylase enzymes, and studies have explored the changes in the redox properties and absorption spectrum upon protonation of the qdt ligand.<sup>14</sup> The only reported case of luminescence from a complex of qdt involves Zn(qdt)<sub>2</sub><sup>2-</sup>, which was found to be emissive at 77 K in rigid media.<sup>15</sup> The present report describes the complexes Pt(phen)-(qdt), Pt(COD)(qdt), and (TBA)<sub>2</sub>[Pt(qdt)<sub>2</sub>], shown below, along



- (9) Bevilacqua, J. M.; Zuleta, J. A.; Eisenberg, R. *Inorg. Chem.* **1993**, *32*, 3689–3693.  
 (10) Bevilacqua, J. M.; Zuleta, J. A.; Eisenberg, R. *Inorg. Chem.*, in press.  
 (11) Zuleta, J. A.; Bevilacqua, J. M.; Proserpio, D. M.; Harvey, P. D.; Eisenberg, R. *Inorg. Chem.* **1992**, *31*, 2396.  
 (12) Burke, R. W.; Deardorff, E. R. *Talanta* **1970**, *17*, 255–264.  
 (13) Ryabushko, O. P.; Pilipenko, A. T.; Batkovskaya, L. A.; Savin, Y. S. *Ukr. Khim. Zh.* **1988**, *54*, 1172–1176.  
 (14) Boyde, S.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1991**, 713.  
 (15) Fernandez, A.; Kisch, H. *Chem. Ber.* **1984**, *117*, 3102.

with the 6,7-dimethylquinoxaline-2,3-dithiolate (dmqdt) analogs in terms of their luminescent properties. Significant differences in the excited-state behavior of these complexes are observed, and the relationship of these states to those of other related dithiolate complexes is discussed.

## Experimental Section

**Materials, Methods, and Preparations.** The compounds K<sub>2</sub>PtCl<sub>4</sub> (Johnson-Matthey), tetra-*n*-butylammonium (TBA) bromide, 1,2-phenylenediamine, 4,5-dimethyl-1,2-phenylenediamine, phosphorus pentachloride, thiourea (Fisher), 1,5-cyclooctadiene (COD), and 1,10-phenanthroline (phen) were used as received from Aldrich (except where noted) without further purification. Pt(COD)Cl<sub>2</sub> and Pt(phen)Cl<sub>2</sub> were prepared according to literature procedures.<sup>16,17</sup> Syntheses of metal complexes were performed under N<sub>2</sub> using standard inert-atmosphere techniques. Solvents used for spectroscopic studies were purified using standard procedures.<sup>18</sup>

**2,3-Quinoxalinedithiol (H<sub>2</sub>qdt).** This compound was prepared from 2,3-dihydroxyquinoxaline (obtained from the condensation of *o*-phenylenediamine with oxalic acid) using a modification of the procedure described by Bernal.<sup>19</sup> It was found that treatment of 2,3-dihydroxyquinoxaline with phosphorus pentachloride did not effect full conversion to 2,3-dichloroquinoxaline but that the latter compound could be easily extracted with ether and the remaining 2,3-dihydroxyquinoxaline reacted further with additional phosphorus pentachloride. Yields for the conversion to 2,3-quinoxalinedithiol using thiourea in ethanol were found to increase when some of the ethanol was removed under vacuum following the treatment with aqueous NaOH. IR (KBr, cm<sup>-1</sup>): 1611 (m), 1561 (m), 1483 (s), 1359 (s), 1326 (s), 1253 (w), 1145 (vs), 1059 (w), 744 (w), 622 (m), 594 (w), 524 (w). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  7.39 m, 7.24 m, 1.89 s.

**6,7-Dimethyl-2,3-quinoxalinedithiol (H<sub>2</sub>dmqdt).** Ethanol solutions of 4,5-dimethyl-1,2-phenylenediamine (1.0 g) and oxalic acid (0.926 g) were mixed at room temperature and allowed to stir for 15 min. The resulting 6,7-dimethyl-2,3-dihydroxyquinoxaline precipitate was filtered off, washed with EtOH, dried under vacuum, and used without further purification. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  6.46 (s, 2H), 2.01 (s, 6H). Preparation of the dithiol followed the procedure of Bernal with the same modifications described above for H<sub>2</sub>qdt. IR (KBr, cm<sup>-1</sup>): 1615 (m), 1560 (m), 1489 (m), 1354 (m), 1323 (s), 1274 (m), 1135 (vs), 1007 (w), 863 (m), 585 (m). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  7.18 (s, 2H), 2.21 (s, 6H), 1.90 (s, 2H).

**(TBA)<sub>2</sub>[Pt(qdt)<sub>2</sub>].** A 0.080 g sample of K<sub>2</sub>PtCl<sub>4</sub> was dissolved in 25 mL of degassed H<sub>2</sub>O. To this was added a degassed solution of 0.0775 g of H<sub>2</sub>qdt and 0.035 g of NaOH in MeOH. The solution turned bright red after 15 min and was allowed to stir for 45 min. A solution of 0.1243 g of (TBA)Br in 10 mL of H<sub>2</sub>O was then added, and bright red microcrystals of (TBA)<sub>2</sub>[Pt(qdt)<sub>2</sub>] precipitated from solution (174.7 mg, 85% yield). The product was filtered off, washed several times with water and ether, and dried under vacuum. IR (KBr, cm<sup>-1</sup>): 2960 (m), 2932 (m), 2872 (m), 1473 (m), 1363 (s), 1258 (s), 1166 (s), 1119 (s), 1020 (w), 879 (w), 754 (w), 600 (w). <sup>1</sup>H NMR (MeOH-*d*<sub>4</sub>):  $\delta$  7.59 (m, 2H), 7.30 (m, 2H), 3.23 (m, 8H), 1.61 (m, 8H), 1.33 (m, 8H), 0.93 (t, 12H). Anal. Calcd for PtC<sub>48</sub>H<sub>80</sub>N<sub>4</sub>S<sub>4</sub>: C, 54.16; H, 7.58. Found: C, 53.85; H, 7.21.

**(TBA)<sub>2</sub>[Pt(dmqt)<sub>2</sub>].** This complex was prepared using the same procedure as that for (TBA)<sub>2</sub>[Pt(qdt)<sub>2</sub>] described above, except with H<sub>2</sub>dmqdt used in place of H<sub>2</sub>qdt. IR (KBr, cm<sup>-1</sup>): 2960 (m), 2934 (sh), 2873 (w), 1470 (w), 1360 (m), 1254 (w), 1196 (m), 1127 (vs), 674 (w), 579 (w), 549 (w). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  7.28 (s, 2H), 3.15 (m, 8H), 2.27 (s, 6H), 1.54 (m, 8H), 1.28 (m, 8H), 0.91 (t, 12H).

**Pt(COD)(qdt).** A 0.310 g sample of Pt(COD)Cl<sub>2</sub> was suspended in 40 mL of EtOH. To this was added a solution of 0.174 g of H<sub>2</sub>qdt and 0.088 g of NaOH in 40 mL of EtOH. After 10 min, the solution

- (16) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.  
 (17) Hodges, K. D.; Rund, J. V. *Inorg. Chem.* **1975**, *14*, 525.  
 (18) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, U.K., 1988.  
 (19) Theriot, L. J.; Ganguli, K. K.; Kavarnos, S.; Bernal, I. *J. Inorg. Nucl. Chem.* **1969**, *31*, 3133–3140.

turned to a clear orange color and was allowed to stir for another 35 min. The solvent was removed under vacuum, and the bright yellow-orange product was dissolved in  $\text{CH}_2\text{Cl}_2$  and recrystallized from hexanes (353.5 mg, 86% yield). IR (KBr,  $\text{cm}^{-1}$ ): 2920 (m), 2874 (m), 1629 (m), 1449 (m), 1367 (m), 1337 (w), 1259 (s), 1179 (s), 1121 (vs), 1007 (w), 758 (m), 601 (m).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.95 (m, 2H), 7.55 (m, 2H), 5.55 (s with Pt satellites, 4H,  $^2J_{\text{Pt-H}} = 56$  Hz, vinyl H), 2.66–2.53 (m, 8H). Anal. Calcd for  $\text{PtC}_{16}\text{H}_{16}\text{N}_2\text{S}_2$ : C, 38.78; H, 3.25. Found: C, 38.93; H, 3.21.

**Pt(COD)(dmqdt).** This complex was prepared using the same procedure as for Pt(COD)(qdt) described above. IR (KBr,  $\text{cm}^{-1}$ ): 2920 (m), 2979 (m), 2828 (m), 1371 (w), 1339 (w), 1245 (s), 1204 (s), 1134 (vs), 1002 (m), 870 (m), 580 (m).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.70 (s, 2H), 5.54 (s with Pt satellites, 4H,  $^2J_{\text{Pt-H}} = 53$  Hz, vinyl H), 2.65–2.52 (m, 8H), 2.41 (s, 6H).

**Pt(phen)(qdt).** To a 0.0750 g sample of Pt(phen) $\text{Cl}_2$  suspended in 30 mL of  $\text{CH}_2\text{Cl}_2$  was added a solution of 0.0540 g of  $\text{H}_2\text{qdt}$  and 0.025 g of NaOH in 15 mL of MeOH. The reaction mixture was stirred at room temperature for 2 h, during which time a bright red-orange precipitate formed. This product was filtered off, and washed with ether and pentane, and dried under vacuum at 40 °C (75.3 mg, 79% yield). IR (KBr,  $\text{cm}^{-1}$ ): 1629 (w), 1554 (w), 1493 (w), 1431 (m), 1367 (m), 1257 (s), 1126 (vs), 1119 (vs), 836 (m), 748 (m), 709 (m), 601 (m).  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ ):  $\delta$  9.31 (d, 2H), 9.07 (d, 2H), 8.33 (s, 2H), 8.23 (dd, 2H), 7.78 (m, 2H), 7.51 (m, 2H). Anal. Calcd for  $\text{PtC}_{20}\text{H}_{12}\text{N}_4\text{S}_2$ : C, 42.33; H, 2.13. Found: C, 42.42; H, 2.04.

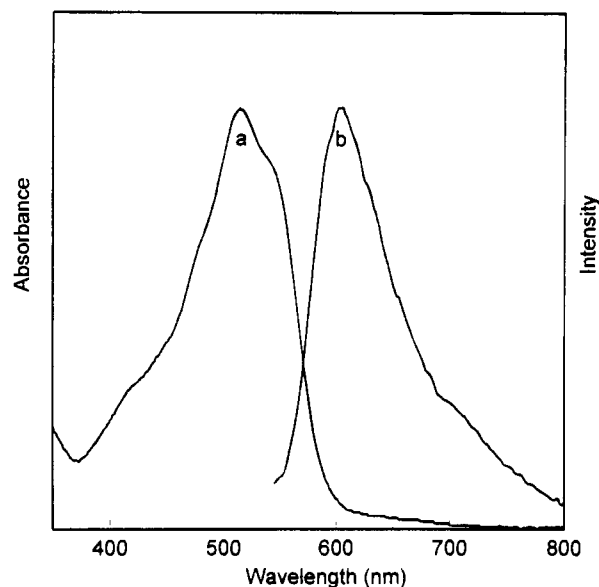
**Pt(phen)(dmqdt).** This complex was prepared using the same procedure as for Pt(phen)(qdt) described above, starting with  $\text{H}_2\text{dmqdt}$ . IR (KBr,  $\text{cm}^{-1}$ ): 1541 (m), 1431 (m), 1368 (w), 1250 (s), 1203 (s), 1133 (vs), 1043 (w), 1002 (w), 839 (m), 711 (m), 581 (m).  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ ):  $\delta$  9.30 (d, 2H), 9.06 (d, 2H), 8.32 (s, 2H), 8.22 (m, 2H), 7.56 (s, 2H), 2.07 (s, 6H).

**Spectroscopic Characterization.**  $^1\text{H NMR}$  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 internal solvent peaks ( $\text{DMSO-}d_6$ ,  $\delta$  2.49;  $\text{CDCl}_3$ ,  $\delta$  7.24; MeOH- $d_4$ ,  $\delta$  3.30). Infrared spectra were recorded on a Mattson Galaxy 6020 FTIR spectrophotometer, and samples were in KBr pellets. Absorption spectra were recorded on a Hitachi U2000 UV–visible spectrophotometer. Room-temperature and low-temperature emission measurements were performed on a Spex Fluorolog fluorescence spectrophotometer using a 1 cm  $\times$  1 cm quartz fluorescence cell and a liquid nitrogen dewar equipped with quartz windows. Quantum yields were calculated relative to absorbance-matched samples of Ru(bpy) $_3\text{Cl}_2$  in degassed  $\text{H}_2\text{O}$  ( $\Phi_{\text{em}}^{298\text{K}} = 0.042 \pm 0.002$ )<sup>20</sup> or in 4:1 EtOH/MeOH ( $\Phi_{\text{em}}^{77\text{K}} = 0.376 \pm 0.036$ ).<sup>21</sup> Absolute accuracy of  $\Phi_{\text{em}}$  at 77 K is  $\pm 30\%$ . Room-temperature lifetimes were measured by single-photon counting, as described elsewhere.<sup>22</sup> Low-temperature emission spectra were recorded in MeOH/EtOH (2:5 v/v), DMF ( $\text{DMF}/\text{CH}_2\text{Cl}_2/\text{MeOH}$  in 1:1:1 v/v/v), or butyronitrile solvent glasses, as specified.

**Electrochemical Measurements.** Cyclic voltammograms were measured using a Cypress Systems CYSY-IR potentiostat driven by Computer-Controlled Electroanalytical System software (CS-1087) on a personal computer. The cell consisted of a glassy-carbon (working) electrode, a Ag wire (reference) electrode, and a Pt wire (auxiliary) electrode in a single compartment.  $(\text{TBA})\text{PF}_6$  (0.1 M) in degassed DMF was used as the electrolyte, and the ferrocene/ferrocenium couple at 0.40 V vs NHE was used to calibrate the cell potential.<sup>23</sup>

## Results and Discussion

**Syntheses.** The ligand 2,3-quinoxalinedithiol was prepared by the method previously described by Bernal.<sup>19</sup> This method was extended to the preparation of 6,7-dimethylquinoxaline-2,3-dithiol by using 4,5-dimethyl-1,2-phenylenediamine in the condensation reaction with oxalic acid. Complexes containing



**Figure 1.**  $(\text{TBA})_2[\text{Pt}(\text{qdt})_2]$  (a) absorption and (b) emission in methanol at 298 K.

the dmqdt ligand were prepared for the purpose of enhancing the solubility of the chromophores for studies of solution luminescence and excited state quenching; however only a modest increase in solubility was obtained. Only the qdt complexes will be focused on below for illustrative purposes.

The preparation of  $(\text{TBA})_2[\text{Pt}(\text{qdt})_2]$  was previously reported by Bernal starting with platinum chloride.<sup>19</sup> A different procedure is described here using  $\text{K}_2\text{PtCl}_4$  as the starting material. The dianionic Pt(II) bis qdt complexes are easily protonated (*vide infra*) so small amounts of base were usually added to aqueous solutions of the complex during workup and manipulation, and solid samples were stored over KOH. Solutions are sensitive to prolonged exposure to air and light, so samples were freshly prepared prior to spectroscopic investigations.

The mixed-ligand Pt(II) complexes were prepared using methods previously reported for the synthesis of Pt(COD)(SS) and Pt(NN)(SS) complexes starting with the corresponding dichloro precursor.<sup>9,22</sup> The synthesis of Pt(phen)(qdt) was best done in  $\text{CH}_2\text{Cl}_2/\text{methanol}$  rather than in the acetone/methanol combination reported for other Pt(NN)(SS) complexes,<sup>9–11</sup> as the latter solvent system led to the formation of significant amounts of  $\text{Pt}(\text{qdt})_2^{2-}$ . In contrast with  $(\text{TBA})_2[\text{Pt}(\text{qdt})_2]$ , solutions of the mixed-ligand complexes are stable in air and light over long periods of time and do not need to be kept under basic conditions.

All of the qdt complexes display a characteristic set of multiplets in their respective  $^1\text{H NMR}$  spectra corresponding to the AA'XX' spin system of the aromatic protons on the quinoxaline ring. In addition, the infrared spectra display a characteristic set of very sharp and intense stretches of the quinoxaline ring between 1370 and 1110  $\text{cm}^{-1}$ .

**Electronic Absorption Spectra.** (a)  $(\text{TBA})_2[\text{Pt}(\text{qdt})_2]$ . The absorption spectrum of  $(\text{TBA})_2[\text{Pt}(\text{qdt})_2]$  in MeOH is shown in Figure 1. The visible region is dominated by an intense feature ( $\epsilon = 25\,000$   $\text{L mol}^{-1} \text{cm}^{-1}$ ) centered around 510 nm ( $\sim 19\,600$   $\text{cm}^{-1}$ ), which displays only a slight bathochromic shift of 350  $\text{cm}^{-1}$  between benzene and DMSO. In aprotic solvents the band possesses two well-resolved maxima separated by  $\sim 1200$   $\text{cm}^{-1}$ , although in protic solvents the profile does broaden slightly and shift to higher energy. The energy and shape of this band are similar to those of the related complex  $(\text{TBA})_2[\text{Pt}(\text{mnt})_2]$  ( $\lambda_{\text{max}} = 474$  nm (21 100  $\text{cm}^{-1}$ ),  $\epsilon = 3470$   $\text{L mol}^{-1} \text{cm}^{-1}$  in  $\text{CH}_3\text{CN}$ ),<sup>24</sup>

(20) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853.

(21) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 2841.

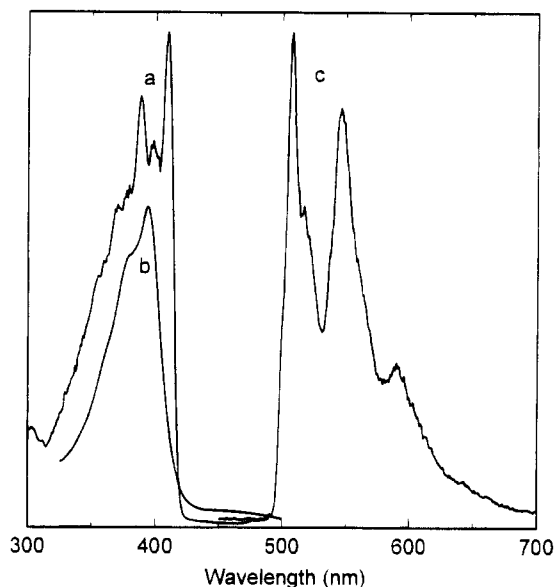
(22) Zuleta, J. A.; Burberry, M. S.; Eisenberg, R. *Coord. Chem. Rev.* **1990**, *97*, 47–64.

(23) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854–2855.

although the molar extinction coefficient is over 7 times greater for  $\text{Pt}(\text{qdt})_2^{2-}$ .

The assignment of the orbitals involved in this electronic transition is based on the energy and molar absorptivity data, as well as comparison with data for other metal bis(dithiolate) complexes. The uncoordinated quinoxaline-2,3-dithiol ligand possesses absorption band maxima at 384, 404, 428, and 455 nm but no absorbance at wavelengths longer than 485 nm. Moreover, the molar absorptivity of the 510 nm band for  $\text{Pt}(\text{qdt})_2^{2-}$  is too large for a metal-centered d-d transition. Both of these facts support a charge-transfer assignment of this transition. Comparison of the visible bands of  $\text{Pt}(\text{qdt})_2^{2-}$  with those for  $\text{Pd}(\text{qdt})_2^{2-}$  ( $\lambda_{\text{max}} = 441 \text{ nm}$ ,  $\epsilon = 21\,300 \text{ L mol}^{-1} \text{ cm}^{-1}$  in MeOH) and  $\text{Ni}(\text{qdt})_2^{2-}$  ( $\lambda_{\text{max}} = 540 \text{ nm}$ ,  $\epsilon = 17\,900 \text{ L mol}^{-1} \text{ cm}^{-1}$  in MeOH) indicates metal orbital involvement in the transition.<sup>25</sup> The ordering of the energies as  $\text{Pd(II)} > \text{Pt(II)} \approx \text{Ni(II)}$  is in accordance with the shifts of MLCT band energies observed for several other homologous series of Pt(II), Pd(II), and Ni(II) square-planar complexes containing cyanide and dithiolate ligands.<sup>24,26-28</sup> Shupack *et al.* characterized the intense visible absorption band for  $\text{Pt}(\text{mnt})_2^{2-}$  as a  $d(\text{Pt})-\pi^*(\text{mnt})$  MLCT involving a HOMO which is a metal d orbital and a LUMO which is a dithiolate  $\pi^*$  orbital.<sup>24</sup> Molecular orbital calculations, infrared (IR) spectroscopy, electron-spin resonance spectroscopy (ESR), and X-ray photoelectron spectroscopy (XPS) have been used to aid in the assignment of the electronic structure of metal bis(dithiolate) complexes. Molecular orbital calculations have been reported for several complexes using a variety of methods, the results of which indicate that the lowest energy charge-transfer state involves a HOMO which is a mixture of dithiolate ( $\pi$ ) and metal (d) orbital character, but the relative contributions are sensitive to both the metal ion and the dithiolate chelate as well as the charge of the complex.<sup>24,29-33</sup> The IR, XPS, and ESR data further support an assignment of a HOMO which is a mixture of dithiolate and metal character and a LUMO which is dithiolate-based.<sup>32,34,35</sup> In light of these results, Güntner and Gliemann have assigned the transition for  $\text{Pt}(\text{mnt})_2^{2-}$  as one which involves a HOMO having a large ligand component and small metal component and a LUMO of  $\pi^*(\text{mnt})$  character.<sup>36</sup> Our conclusion, based on the observations concerning the electronic transitions for  $\text{Pt}(\text{qdt})_2^{2-}$  and the results from studies of other metal bis(dithiolate) complexes, is that the lowest-energy excited state is a mixture of MLCT and dithiolate intraligand (IL) character. The term charge-transfer-to-dithiolate will be used to describe this electronic transition.

Significant changes occur in the absorption spectrum of  $\text{Pt}(\text{qdt})_2^{2-}$  if the solution pH is lowered below 7. A new low-energy band emerges at 590 nm ( $16\,950 \text{ cm}^{-1}$ ), and the solution changes from bright red to deep blue. The nature of these spectroscopic changes is interpreted as arising from protonation of the quinoxalinedithiolate ligand at the imine position, and a



**Figure 2.**  $\text{Pt}(\text{COD})(\text{qdt})$  (a) excitation (MeOH/EtOH, 77 K, 509 nm emission), (b) absorption (MeOH, 298 K), and (c) emission (MeOH/EtOH, 77 K, 360 nm excitation).

full investigation of the acid-base behavior of the ground and excited states of this complex will be published separately.<sup>37</sup>

**(b)  $\text{Pt}(\text{COD})(\text{qdt})$ .** The absorption spectrum of  $\text{Pt}(\text{COD})(\text{qdt})$  is shown in Figure 2 and is composed of an intense absorption band with maxima at 376 and 392 nm ( $26\,600$  and  $25\,510 \text{ cm}^{-1}$  respectively, with  $\epsilon = 13\,900$  and  $16\,500 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and a weaker low energy shoulder at 425 nm ( $23\,530 \text{ cm}^{-1}$ ,  $\epsilon = 1990 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). These bands are almost identical in shape and close in extinction coefficient to those of the related complex  $\text{Pt}(\text{COD})(\text{mnt})$ , although they lie approximately  $3500 \text{ cm}^{-1}$  lower in energy. These transitions undoubtedly involve the qdt ligand, since transitions in this region are absent for both 1,5-cyclooctadiene and  $\text{Pt}(\text{COD})\text{Cl}_2$ , and metal involvement is supported by the fact that the complex spectrum differs from that of  $\text{H}_2\text{qdt}$  or  $\text{Na}_2\text{qdt}$ . Therefore this transition is assigned as charge-transfer-to-dithiolate having orbital contributions similar to those for the  $\text{Pt}(\text{qdt})_2^{2-}$  complex described above. The shift to higher energy relative to the CT band of the  $\text{Pt}(\text{qdt})_2^{2-}$  complex is consistent with the increased stability of d orbital energies in going from a dianionic complex to a neutral species. Assignment of the low-energy shoulder is uncertain, although either a d-d or a spin-forbidden CT transition is possible.

**(c)  $\text{Pt}(\text{phen})(\text{qdt})$ .** In contrast to  $\text{Pt}(\text{qdt})_2^{2-}$  and  $\text{Pt}(\text{COD})(\text{qdt})$ , the mixed-ligand diimine dithiolate complex  $\text{Pt}(\text{phen})(\text{qdt})$  possesses an intense band at lower energy which is strongly solvent-dependent. The absorption spectra in six different solvents are presented in Figure 3, displaying the solvatochromic behavior of the lower-energy feature which shifts from 498 nm ( $20\,080 \text{ cm}^{-1}$ ) in chloroform to 458 nm ( $21\,830 \text{ cm}^{-1}$ ) in DMSO. A study of this solvatochromism was conducted in 10 different aprotic solvents. The energy maxima correlate well with the  $E^*_{\text{MLCT}}$  solvent scale,<sup>38</sup> as shown in Figure 4, and the slope indicates that this transition involves a significant change in dipole moment between a polar ground state and a less polar excited state which is characteristic of other  $\text{Pt}(\text{NN})(\text{SS})$  complexes.<sup>11</sup> A detailed study of the solvatochromic transition for  $\text{Pt}(\text{diimine})(\text{dithiolate})$  complexes, where dithiolate = mnt and ecda, revealed that the LUMO or acceptor orbital is clearly

(24) Shupack, S. I.; Billig, E.; Clark, R. J. H.; Williams, R.; Gray, H. B. *J. Am. Chem. Soc.* **1964**, *86*, 4594.

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

(26) Gray, H. B.; Bullhausen, C. J. *J. Am. Chem. Soc.* **1963**, *85*, 260.

(27) Werden, B. G.; Billig, E.; Gray, H. B. *Inorg. Chem.* **1966**, *5*, 78.

(28) Fackler, J. P., Jr.; Coucouvanis, D. *J. Am. Chem. Soc.* **1966**, *88*, 3913.

(29) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1965**, *87*, 3585.

(30) Blomberg, M. R. A.; Wahlgren, U. *Chem. Phys.* **1980**, *49*, 117.

(31) Zális, S.; Vlcek, A. A. *Inorg. Chim. Acta* **1982**, *58*, 89.

(32) Sano, M.; Adachi, H.; Yamatera, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2636.

(33) Clemenson, P. I. *Coord. Chem. Rev.* **1990**, *106*, 171-203.

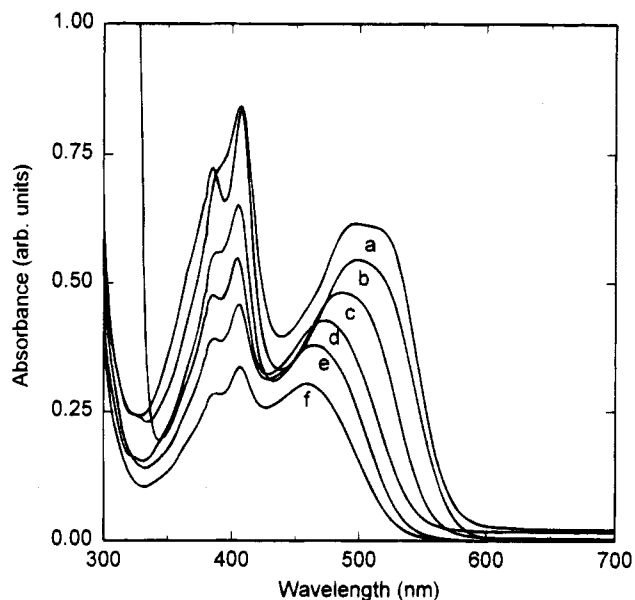
(34) Schläpfer, C. W.; Nakamoto, K. *Inorg. Chem.* **1975**, *14*, 1338.

(35) Kirmse, R.; Dietzsch, W.; Solov'ev, B. V. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1157-1160.

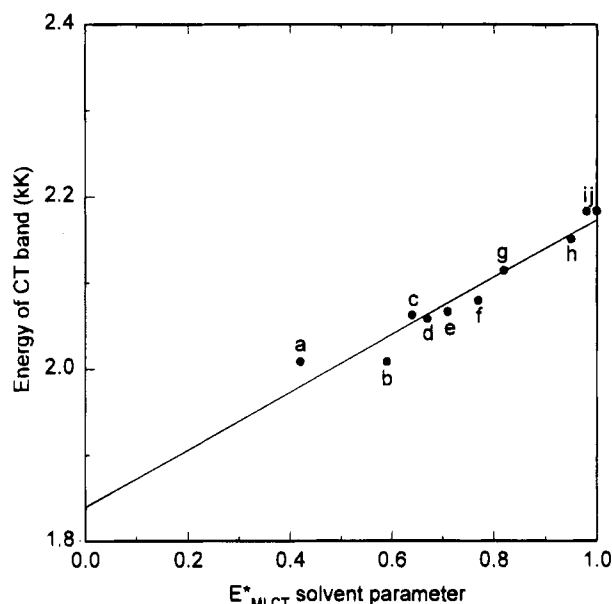
(36) Güntner, W.; Gliemann, G. *J. Phys. Chem.* **1990**, *94*, 618-624.

(37) Cummings, S. D.; Eisenberg, R. *Inorg. Chem.*, in press.

(38) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 3825.



**Figure 3.** Pt(phen)(qdt) absorption in (a) chloroform, (b) tetrahydrofuran, (c) dichloromethane, (d) acetone, (e) *N,N*-dimethylformamide, and (f) dimethyl sulfoxide.



**Figure 4.** Plot of the energy of the CT band maxima ( $10^3 \text{ cm}^{-1}$ ) versus the  $E^*_{\text{MLCT}}$  solvent parameter for (a) chloroform, (b) tetrahydrofuran, (c) 1,2-dichloroethane, (d) dichloromethane, (e) 3-pentanone, (f) pyridine, (g) acetone, (h) *N,N*-dimethylformamide, (i) acetonitrile, and (j) dimethyl sulfoxide.

$\pi^*$ (diimine) although molecular orbital calculations show that low-lying  $\pi^*$ (dithiolate) orbitals are close in energy. The nature of the HOMO or donor orbital for the solvatochromic bands in these complexes is less clear. Both systematic substitution and molecular orbital calculations reveal that the HOMO contains significant Pt(d), S(p), and dithiolate  $\pi$  characters which vary depending on the dithiolate. On the basis of these studies, the solvatochromic transition was assigned as Pt(d)/S(p)- $\pi^*$ (diimine) or mixed-metal/ligand-to-ligand charge transfer (MMLL'CT). For Pt(phen)(qdt) a similar assignment holds, with the LUMO composed of  $\pi^*$ (phen) and a HOMO of mixed metal-qdt composition. We will therefore designate the transition as charge-transfer-to-diimine. In earlier studies of Ni(II), Pd(II), and Pt(II) diimine dithiolate complexes by Dance<sup>39</sup>

and Vogler<sup>40</sup> and recent studies by Crosby<sup>41</sup> of related  $d^{10}$  Zn(II) complexes, similar solvatochromic transitions were seen and assigned as ligand-to-ligand charge transfers (LLCT). However, it is evident that the solvent-dependent transitions of the diimine dithiolate complexes reflect significant metal orbital involvement in the HOMO on the basis of both experimental and computational results.

The feature which lies at higher energy in the spectrum of Pt(phen)(qdt) has two resolved maxima in DMF at 386 nm ( $25\,907 \text{ cm}^{-1}$ ) and 405 nm ( $24\,691 \text{ cm}^{-1}$ ), the energies of which do not shift in other solvents. The energy difference of  $1215 \text{ cm}^{-1}$  for these two bands is very similar to those of both  $(\text{TBA})_2[\text{Pt}(\text{qdt})_2]$  ( $1219 \text{ cm}^{-1}$  in THF) and Pt(COD)(qdt) ( $1156 \text{ cm}^{-1}$  in MeOH) CT bands described above. The feature is therefore assigned to a charge-transfer-to-dithiolate transition in which the unoccupied orbital is a  $\pi^*$  orbital of the qdt ligand rather than of the phen ligand. This assignment is consistent with the expected lowering of the CT band energy for the complexes Pt(COD)(qdt), Pt(phen)(qdt), and Pt(qdt)<sub>2</sub><sup>2-</sup>, in which the metal d orbitals corresponding to the HOMO's have increasingly higher energies.

**Emission Spectra.** (a)  $(\text{TBA})_2[\text{Pt}(\text{qdt})_2]$ . Emission from  $(\text{TBA})_2[\text{Pt}(\text{qdt})_2]$  is observed in both room-temperature fluid solution and low-temperature (77 K) matrices. The 298 K emission in MeOH shown in Figure 1 is a featureless band at 606 nm which is very weak at ambient conditions with an emission quantum yield  $\Phi_{\text{em}}$  of  $\sim 10^{-5}$ . This emission is blue-shifted from the 775 nm emission of the corresponding  $(\text{TBA})_2[\text{Pt}(\text{mnt})_2]$  complex in MeOH and has a comparable intensity.<sup>25</sup> Although the emission intensity is not quenched by either oxygen or small amounts of water, the emission band shape and intensity do change slightly with solvent, but no general trend with solvent polarity or other solvent properties is apparent. As with the absorption features, there is a significant change in the emission profile with decreased solution pH, with a new feature emerging at 728 nm. This new emission is attributed to the protonated form of the complex and will be reported separately as part of the studies of the pH-dependent spectroscopic properties of this system.<sup>37</sup>

The emission from  $(\text{TBA})_2[\text{Pt}(\text{qdt})_2]$  at 77 K in frozen MeOH/EtOH glass has a  $\Phi_{\text{em}}$  of 0.044 and displays a small amount of structure, although it lacks the resolution necessary to accurately assign a vibrational progression. The emission from Pt(qdt)<sub>2</sub><sup>2-</sup> is tentatively assigned to originate from a CT state of orbital character similar to that of the lowest energy CT absorption described above. This is supported by the broad nature of the emission and comparison with the emission spectra from both Pt(mnt)<sub>2</sub><sup>2-</sup> and Zn(qdt)<sub>2</sub><sup>2-</sup>, which show a dependence on both the metal center and the dithiolate for the observed emission energies.<sup>15,25</sup> The sub-nanosecond solution lifetimes and quantum yield of  $\sim 10^{-5}$  lead to an estimated natural radiative lifetime,  $\tau_0$ , on the order of 10  $\mu\text{s}$  or less, suggesting a formally spin-forbidden process for a third-row transition metal complex. Further work on the emission from Pt(qdt)<sub>2</sub><sup>2-</sup> and other homoleptic Pt(II) bis(dithiolate) complexes is being investigated.<sup>25</sup>

(b) Pt(COD)(qdt). Emission from Pt(COD)(qdt) is observed in frozen solvent glass at 77 K but not in fluid solutions at room temperature. The excitation and emission spectra in MeOH/EtOH glass are shown in Figure 2. The complex is highly emissive at 77 K, with a quantum yield for emission of 0.58.

(40) Vogler, A.; Kunkely, H.; Hlavatsch, J.; Merz, A. *Inorg. Chem.* **1984**, *23*, 506.

(41) Crosby, G. A.; Highland, R. G.; Truesdell, K. A. *Coord. Chem. Rev.* **1990**, 8916.

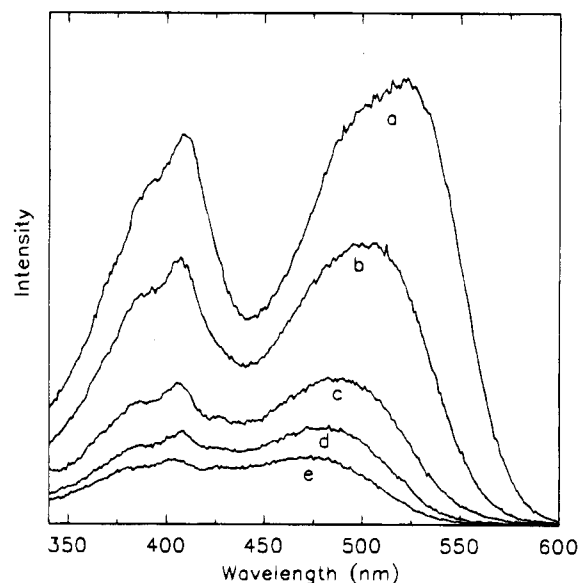
(39) Miller, T. R.; Dance, G. *J. Am. Chem. Soc.* **1973**, *95*, 6790.

The highest energy emission maximum is found at 508 nm, which is blue-shifted  $\sim 2500\text{ cm}^{-1}$  from the emission maximum for Pt(COD)(mnt) even though its absorption maximum is red-shifted  $\sim 3500\text{ cm}^{-1}$  from that of Pt(COD)(mnt). Assuming that the emission for these complexes is a spin-forbidden phosphorescence, which appears to be true for all of the emissive transition metal dithiolate complexes studied thus far, then this difference in the relative shift between absorption and emission energy maxima is reflective of the difference in the relative energies of the singlet and triplet CT states of the qdt and mnt complexes. In fact, the same trend is observed when the absorption and emission maxima for Pt(mnt) $_2^{2-}$  and Pt(qdt) $_2^{2-}$  are compared, specifically that the absorption maximum of Pt(qdt) $_2^{2-}$  is red-shifted  $1260\text{ cm}^{-1}$  from that of Pt(mnt) $_2^{2-}$  but the emission maximum for Pt(qdt) $_2^{2-}$  is blue-shifted  $3600\text{ cm}^{-1}$  from the emission maximum of Pt(mnt) $_2^{2-}$ .

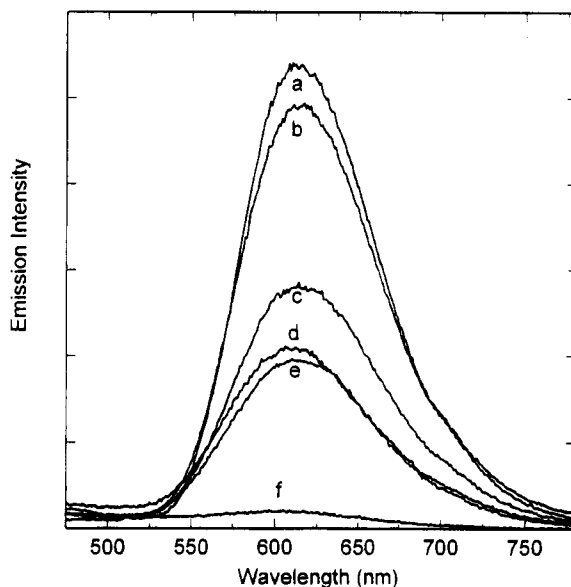
Unlike that of (TBA) $_2$ [Pt(qdt) $_2$ ] or Pt(phen)(qdt) (*vide infra*), the emission profile of Pt(COD)(qdt) is highly structured, with at least two vibrational progressions discernible at  $1370$  and  $340\text{ cm}^{-1}$ . The larger energy spacing of  $1370\text{ cm}^{-1}$  is the dominant feature of the vibrational structure and corresponds to a C=C stretch of the quinoxaline ring. This stretching mode is observed at  $1367\text{ cm}^{-1}$  in the IR spectrum of Pt(COD)(qdt), at  $1359\text{ cm}^{-1}$  for free quinoxaline-2,3-dithiol, and at  $1362\text{ cm}^{-1}$  for (TBA) $_2$ [Pt(qdt) $_2$ ]. In addition, a  $1395\text{ cm}^{-1}$  stretch is observed in the resonance Raman spectrum of Pt(COD)(qdt). The structured excitation spectrum shows a vibrational spacing of  $1323\text{ cm}^{-1}$ , corresponding to an excited state C=C stretching frequency which is lower in energy than the ground state vibration. This result is consistent with a CT excited state that involves a  $\pi^*$  orbital of the quinoxalinedithiolate which has C=C antibonding character. Vibrational structure has been seen in the emission spectra of related mnt complexes.<sup>42</sup> In each case a major progression lies in the region of  $1400\text{ cm}^{-1}$  corresponding to the localized C=C stretch of the mnt ligand. However, in analogous metal complexes containing the 1,1-dithiolate ecda, which has a C=C double bond exocyclic to the chelate ring, vibrational structure is completely absent, suggesting that the nature of the dithiolate strongly influences vibronic coupling in the excited state of these chromophores. The emission from Pt(COD)(qdt) is thus very similar to that observed for other Pt(II) dithiolate complexes with COD, phosphine, or phosphite ligands which exhibit emission energies that depend on the electron density at the metal center and emission structure that is characteristic of the dithiolate. On the basis of these observations, the emission for Pt(COD)(qdt) is therefore assigned to originate from a charge-transfer-to-dithiolate excited state.

(c) **Pt(phen)(qdt)**. In contrast to the above systems, Pt(phen)(qdt) is highly emissive in fluid solution ( $\Phi_{\text{em}} = 2.99 \times 10^{-3}$  in chloroform). The emission is quenched by oxygen, so samples were routinely degassed. The emission profile at room temperature is a broad band (fwhm =  $2443\text{ cm}^{-1}$ ) centered around  $612\text{ nm}$  ( $16340\text{ cm}^{-1}$ ) having no vibronic structure. Low-temperature samples do exhibit structured emission, with two well-resolved maxima at  $563\text{ nm}$  ( $17760\text{ cm}^{-1}$ ) and  $607\text{ nm}$  ( $16475\text{ cm}^{-1}$ ) in butyronitrile glass at  $77\text{ K}$ . This corresponds to an energy spacing of  $1288\text{ cm}^{-1}$ , which is close to the observed  $1257\text{ cm}^{-1}$  qdt ring mode stretching frequency observed in the solid state IR spectrum.

The excitation spectra of Pt(phen)(qdt) were measured in five different solvents with emission collected at  $600\text{ nm}$ , and the results are presented in Figure 5. The excitation spectra closely



**Figure 5.** Pt(phen)(qdt) excitation spectra in (a) chloroform, (b) dichloromethane, (c) acetone, (d) *N,N*-dimethylformamide, and (e) acetonitrile. Emission was collected at  $620\text{ nm}$  for all samples.



**Figure 6.** Pt(phen)(qdt) emission spectra in (a) chloroform, (b) dichloromethane, (c) acetone, (d) *N,N*-dimethylformamide, (e) acetonitrile, and (f) dimethyl sulfoxide using  $380\text{ nm}$  excitation for all samples.

match absorption spectra in both shape and energy and display the same solvatochromic shift from low energy to higher energy with increasing solvent polarity (see Figure 3). However, the emission energy is essentially unaffected by solvent, shifting less than  $8\text{ nm}$  between  $\text{CHCl}_3$  and DMSO solutions. In contrast, the emission intensity is highly solvent-dependent, decreasing substantially with an increase in solvent polarity. Figure 6 shows the relative emission intensities of samples prepared in six solvents of differing polarity. The quantum yields of emission are given in Table 1 and range from  $0.3\%$  in  $\text{CHCl}_3$  to only  $0.01\%$  in DMSO.

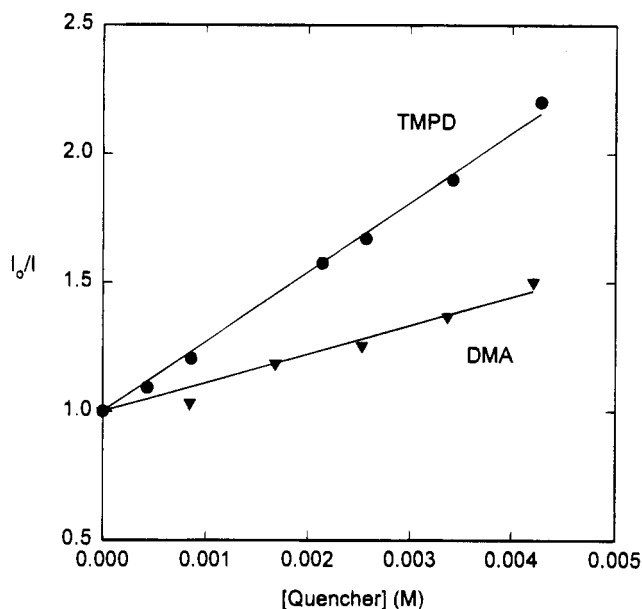
Excited state lifetimes for Pt(phen)(qdt) are also highly solvent-dependent. Decays were fit to single exponentials for all of the solvents, yielding lifetimes ranging from  $32$  to  $138\text{ ns}$ , as shown in Table 1. The lifetimes clearly correlate inversely with solvent polarity, with longer excited state lifetimes observed in less polar solvents. The origin of this solvent-induced quenching can be found by analyzing the calculated radiative

(42) Johnson, C. E.; Eisenberg, R.; Evans, T. R.; Burberry, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1795–1802.

**Table 1.** Emission Quantum Yield and Lifetime Data for Pt(phen)(qdt) in Various Solvents at 25 °C

| solvent                         | $\Phi_{em}$ ( $10^{-3}$ ) <sup>a</sup> | $\tau$ ( $\mu$ s) <sup>b</sup> | $\tau_0$ ( $\mu$ s) <sup>c</sup> | $k_r$ ( $\mu$ s <sup>-1</sup> ) <sup>d</sup> | $k_{nr}$ ( $\mu$ s <sup>-1</sup> ) <sup>e</sup> |
|---------------------------------|--|--------------------------------|----------------------------------|--|---|
| CHCl <sub>3</sub>               | 3.0                                    | 0.117                          | 39 ± 2.0                         | 0.026 ± 0.001                                | 8.5 ± 0.07                                      |
| CH <sub>2</sub> Cl <sub>2</sub> | 2.7                                    | 0.087                          | 32 ± 1.6                         | 0.031 ± 0.002                                | 11.5 ± 0.1                                      |
| acetone                         | 1.5                                    | 0.055                          | 36 ± 1.9                         | 0.028 ± 0.002                                | 18.1 ± 0.3                                      |
| DMF                             | 1.1                                    | 0.037                          | 33 ± 1.9                         | 0.031 ± 0.002                                | 27.0 ± 0.7                                      |
| CH <sub>3</sub> CN              | 1.1                                    | 0.030                          | 28 ± 1.7                         | 0.036 ± 0.002                                | 33.3 ± 1.1                                      |
| DMSO                            | 0.1                                    |                                |                                  |  |   |

<sup>a</sup> Excited at 400 nm; ±5%. <sup>b</sup> Excited at 380 nm; ±1 ns. <sup>c</sup> Calculated from  $\tau_0 = \tau/\Phi_{em}$ . <sup>d</sup> Calculated from eq 1. <sup>e</sup> Calculated from eq 2.

**Figure 7.** Stern–Volmer plot of reductive quenching of Pt(phen)(qdt) emission in DMF using TMPD (●) and DMA (▼). Samples were excited at 400 nm.

and nonradiative rate constants which are given by eqs 1 and 2

$$k_r = \Phi_{em}/\tau \quad (1)$$

$$k_{nr} = 1/\tau - \Phi_{em}/\tau \quad (2)$$

assuming unit efficiency of intersystem crossing to the triplet state. Analysis of the results given in Table 1 shows only a 55% increase in the radiative rate constant in going from chloroform to acetonitrile solutions but a 330% increase in the nonradiative rate constant between the same solvents. Clearly, polar solvents are efficient in quenching the excited state of Pt(phen)(qdt) via nonradiative pathways.

In addition to quenching by oxygen or solvent, electron-transfer quenching has been observed for Pt(phen)(qdt). Quenching studies using reductive quenchers *N,N*-dimethylaniline (DMA) and *N,N,N',N'*-tetramethylphenylenediamine (TMPD) were conducted in DMF solutions. The triplet energies of these aromatic systems are significantly higher than that estimated for the excited state of Pt(phen)(qdt) at 51 kcal/mol, allowing for only electron transfer quenching and not energy transfer, which has been seen for related Pt(NN)(SS) complexes with metallocene quenchers.<sup>10</sup> Stern–Volmer analyses of the quenching data for both DMA and TMPD yielded Stern–Volmer constants,  $K_{SV}$ , of 111 (DMA) and 270 (TMPD), from the plots of Figure 7. From these results and a solution lifetime of 37 ns in DMF, quenching rate constants of  $2.8 \times 10^9$  s<sup>-1</sup> (DMA) and  $6.9 \times 10^9$  s<sup>-1</sup> (TMPD) were calculated, indicating that Pt(phen)(qdt)\* oxidizes aromatic amines of appropriate donor ability at rates close the diffusion-controlled limit.

Since Pt(phen)(qdt) appeared to be a strong oxidant in the excited state, an estimation of the excited state reduction potential  $E_{1/2}^*$  was determined from spectroscopic and electrochemical data and the relation

$$E_{1/2}^* = E_{0-0} + E_{1/2} \quad (3)$$

where  $E_{0-0}$  is the 0–0 energy difference between the ground and emissive excited states and  $E_{1/2}$  is the reversible reduction potential of the complex. Using  $E_{0-0}$  of 2.20 eV which was approximated by the energy maximum of the emission at 77 K in butyronitrile and  $E_{1/2}$  of -1.06 V from cyclic voltammetry (*vide infra*), an excited state reduction potential of 1.14 V vs NHE was obtained. This result indicates that Pt(phen)(qdt) is a powerful photooxidant, almost 0.3 V stronger than Ru(bpy)<sub>3</sub><sup>2+</sup>.<sup>43</sup>

Variation of the dithiolate from qdt to dmqdt has only minor effects on the electronic properties of these systems. For example, the energy maximum for emission in DMF is shifted from 612 nm for Pt(phen)(qdt) to 624 nm for Pt(phen)(dmqdt), consistent with the charge-transfer-to-diimine assignment given above in which added electron-donating methyl groups on the dithiolate raise the energy of the HOMO. The differences in the emission energies for (TBA)<sub>2</sub>[Pt(qdt)<sub>2</sub>] and (TBA)<sub>2</sub>[Pt(dmqdt)<sub>2</sub>] are even less pronounced, and the absorption spectra are essentially superimposable.

No emission was detected in either room-temperature solutions or low-temperature solvent glasses for the free ligand H<sub>2</sub>-qdt.

**Electrochemical Studies.** Redox potentials obtained from electrochemical measurements are relevant to a discussion of the nature of the HOMO and LUMO in each of the Pt(II) qdt complexes. Cyclic voltammetry was conducted on (TBA)<sub>2</sub>[Pt(qdt)<sub>2</sub>], Pt(COD)(qdt), and Pt(phen)(qdt) in DMF with 0.10 M (TBA)PF<sub>6</sub> electrolyte. (TBA)<sub>2</sub>[Pt(qdt)<sub>2</sub>] possesses a reversible oxidation wave with  $E_{1/2} = 0.45$  V vs NHE and an irreversible reduction wave at  $E_p = -1.08$  V vs NHE. The ease of oxidation is similar to that of many other dianionic metal bis(dithiolate) complexes, such as (TBA)<sub>2</sub>[Pt(mnt)<sub>2</sub>] for which  $E_{1/2} = 0.21$  V.<sup>44</sup> Pt(COD)(qdt) has an irreversible oxidation wave at  $E_p = 0.94$  V and an irreversible reduction wave at  $E_p = -1.37$  V vs NHE. Pt(phen)(qdt) possesses an irreversible oxidation wave at  $E_p = 0.95$  V and a reversible reduction wave at  $E_{1/2} = -1.06$  V. The neutral nature of these mixed-ligand complexes clearly makes them less easily oxidized relative to the dianionic Pt(qdt)<sub>2</sub><sup>2-</sup>, as seen by the increase in the anodic peak potentials and the irreversibility of the oxidation. The electrochemical reductions of the mixed-ligand complexes differ substantially in their  $E_{1/2}$  values and reversibility, supporting the notion that the LUMO in these systems differs and depends on the nature of the non-dithiolate ligands. This difference was discussed above in terms of the spectroscopic properties of the mixed liquid complexes, and the electrochemical results are totally consistent with those conclusions. Specifically, the facile and reversible nature of the reduction of Pt(phen)(qdt) is consistent with a LUMO which is  $\pi^*(phen)$ , as observed for other transition metal complexes with 1,10-phenanthroline,<sup>45</sup> while for Pt(COD)(qdt) and Pt(qdt)<sub>2</sub><sup>2-</sup>, the LUMO is  $\pi^*(qdt)$ .

(43) Strouse, G. F.; Anderson, P. A.; Shoonover, J. R.; Meyer, T. J.; Keene, F. R. *Inorg. Chem.* **1992**, *31*, 3004.

(44) Davidson, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *Inorg. Chem.* **1964**, *3*, 814.

(45) Juris, A.; Balzani, V.; Barigelli, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

## Conclusions

A set of Pt(II) complexes of quinoxaline-2,3-dithiolate and 6,7-dimethylquinoxaline-2,3-dithiolate have been synthesized and studied in terms of photophysical behavior. Although variation between qdt and dmqdt has only minor effects on the emissive properties, variation in the other ligands among 1,5-cyclooctadiene, 1,10-phenanthroline, and a second qdt ligand significantly alters the charge-transfer and emissive properties. Specifically, variation in the other chelates can lead to differences in (1) the nature of the lowest energy excited state between charge-transfer-to-dithiolate and charge-transfer-to-diimine which possess LUMO's of significantly different orbital character, (2) solvatochromic properties, (3) the quantum yields for emission

ranging from  $<10^{-5}$  to  $10^{-3}$  in ambient solutions, (4) the structure of emission bands, and (5) redox properties. Furthermore, Pt(phen)(qdt) possesses longer solution lifetimes, higher  $\Phi_{em}$ , and a greater excited state reduction potential than any other previously-studied Pt(II) diimine dithiolate complex, indicating that quinoxaline-2,3-dithiolate shows promise for further development of mixed-ligand Pt(NN)(SS) chromophores.

**Acknowledgment.** We wish to thank the Department of Energy, Division of Chemical Sciences, for support of this research and Professor Pierre Harvey for the resonance Raman measurement. A generous loan of platinum salts from Johnson Matthey Aesar/Alpha Co. is also gratefully acknowledged.

IC9408359