

spectra of ^{13}C - and ^{15}N -enriched samples were recorded for spectral widths of 50 and 25 kHz (50000 and 1200-2500 scans), respectively, with acquisition times of 0.328 and 0.655 s and data point resolutions of 3.05 and 1.53 Hz/pt, respectively. Fluorine-19 NMR spectra were recorded for spectral widths of 50 and 100 kHz with acquisition times of 0.082 and 0.164 s and data point resolutions of 3.05 and 6.10 Hz/pt (4500 and 7500 scans), respectively. Nitrogen-15 and -14 NMR spectra were recorded for spectral widths of 25 and 10 kHz with acquisition times of 0.655 and 0.410 s and data point resolutions of 1.53 and 2.44 Hz/pt (1400 and 26000 scans), respectively. Carbon-13 NMR spectra were recorded for a spectral width of 15 kHz with an acquisition time of 0.541 s and data point resolution of 1.85 Hz/pt (3000 scans). Proton spectra were recorded for spectral widths of 800 Hz and 3 kHz with acquisition times of 5.12 and 2.80 s and data point resolutions of 0.098 and 0.357 Hz/pt (64 and 172 scans), respectively.

Pulse widths corresponding to bulk magnetization tip angles of $\sim 90^\circ$ were 22 (^{129}Xe), 2 (^{19}F), 49 (^{14}N), 35 (^{15}N), 7 (^{13}C), and 0.5 μs (^1H). No relaxation delays were applied except in the case of ^{15}N , where a relaxation delay of 10 s was applied. Line-broadening parameters used in exponential multiplication of the free induction decays were set equal to or less than their respective data point resolutions. All line shape functions were Lorentzian with the exception of the ^1H spectra and the ^{129}Xe NMR spectrum of [^{13}C]HC \equiv NXeF $^+$ AsF $_6^-$; in these cases Gaussian line shapes were applied for resolution enhancement.

The respective nuclei were referenced externally to neat samples of XeOF $_4$ (^{129}Xe), CFC $_3$ (^{19}F), CH $_3$ NO $_2$ (^{14}N and ^{15}N), and (CH $_3$) $_4$ Si (^{13}C and ^1H) at 24 $^\circ\text{C}$. Positive chemical shifts were assigned to resonances occurring to high frequency of the reference substance.⁴⁹

For variable-temperature measurements, samples were kept cold (-196 or -78 $^\circ\text{C}$) until immediately prior to their placement in the probe. They were generally warmed only enough to liquify and solubilize the contents and were then quickly placed in the precooled probe. Prior to data accumulation, the tubes were allowed to equilibrate in the probe for periods of several minutes while spinning. Temperatures were periodically

checked by placing a copper-constantan thermocouple into the sampling region of the probe. Temperatures were considered to be accurate to within ± 1 $^\circ\text{C}$.

Raman Spectroscopy. A Coherent Model Innova 90 argon ion laser giving up to 3.5 W of power at 514.5 nm was used to excite the Raman spectra. The spectrometer was a Spex Industries Model 14018 double monochromator equipped with 1800 grooves/mm holographic gratings. Slit widths depended on the scattering efficiency of the sample, laser power, etc. and were set at 100-150 μm . An RCA C31034 phototube detector in conjunction with a pulse count system consisting of pulse amplifier, analyzer, and rate meter (Hamner NA-11, NC-11, and N-780 A, respectively) and a Texas Instruments Model FSOZWBA strip-chart recorder were used to record the spectra. The scanning rates used were 0.2 and 0.5 $\text{cm}^{-1} \text{ s}^{-1}$. The typical power range used was between 0.7 and 1 W. The spectrometer was periodically calibrated by recording the discharge lines from an argon lamp over the spectral range of interest; all the Raman shifts quoted are estimated to be accurate to at least ± 2 cm^{-1} , while the precision of each Raman shift measurement is estimated to be ± 0.2 cm^{-1} .

Cylindrical $1/4$ -in. FEP sample tubes were mounted vertically. The angle between the incident laser beam and sample tube was 45° , and Raman scattered radiation was observed at 45° to the laser beam (90° to the sample tube axis). Low-temperature spectra were recorded at -196 $^\circ\text{C}$ by mounting the sample vertically in an unsilvered Pyrex glass dewar filled with liquid nitrogen. All spectra were obtained directly in $1/4$ -in. FEP reaction vessels. The spectrum of the FEP sample tube was nearly always observed; however, their prominence in the overall spectrum depended on the efficiency of the sample as a Raman scatterer and could be minimized by focusing the laser beam on the sample surface. Lines arising from FEP have been subtracted out of the spectra reported in the tables but not in the figures.

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Multiple-State Emission from Platinum(II) Diimine Dithiolate Complexes. Solvent and Temperature Effects

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The solvent and temperature dependence of the emission of Pt(diimine)(dithiolate) complexes is reported where diimine = 4,4'-dimethyl-2,2'-bipyridine (dmbpy) or 4,7-diphenyl-1,10-phenanthroline (dpphen) and dithiolate = 1-(ethoxycarbonyl)-1-cyanoethylene-2,2'-dithiolate (ecda) or 1-(*tert*-butoxycarbonyl)-1-cyanoethylene-2,2'-dithiolate (tbcda). In fluid solution at room temperature, a single emission band is observed at ~ 16670 cm^{-1} (600 nm) for the complexes Pt(dmbpy)(ecda) (1), Pt(dpphen)(ecda) (2), and Pt(dpphen)(tbcda) (3), which are studied in detail. The radiative quantum yields and lifetimes of the emission decrease with increasing solvent polarity for the three complexes. In DMF/CH $_2$ Cl $_2$ /MeOH the emission intensity for the complexes increases between 298 and 175 K with no change in the emission energy. Between 175 and 165 K the emission undergoes a red shift to ~ 15625 cm^{-1} (640 nm), corresponding to a rigidochromic effect, and below 140 K two new bands appear at higher energies (17000-18500 and 18600-19900 cm^{-1}). The latter bands have a relative separation of 1360 cm^{-1} and are assigned to a π - π^* diimine transition on the basis of their observed lifetime and comparison with PtCl $_2$ (diimine) analogues. Between 80 and 6 K, the lifetime of the 15625- cm^{-1} (640-nm) emission band increases, while, below 50 K, its emission intensity decreases with decreasing temperature, suggesting the presence of closely spaced excited states. From a kinetic analysis of the radiative quantum yield and lifetime data, the low-energy emission is assigned to a charge-transfer manifold of two emitting states separated by 50-60 cm^{-1} .

Introduction

Excited organic molecules almost always emit from the lowest excited state of a given multiplicity. This principle, known as Kasha's rule, does not always apply in the case of transition metal complexes, and a number of exceptions to the rule have been

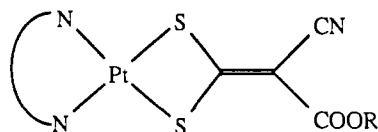
reported. The prime example of this group is Ru(bpy) $_3^{2+}$ (bpy = 2,2'-bipyridine) and its analogues, which Crosby and co-workers have shown to possess a metal-to-ligand charge-transfer (MLCT) manifold of three closely spaced, thermally equilibrated levels.³ Another d 6 system of pseudooctahedral geometry is CpRe(CO) $_2$ L (Cp = η^5 -cyclopentadienyl; L = pyridine, 4-phenylpyridine), which

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has recently been investigated by Lees⁴ and found to emit from several nonequilibrated excited states of different orbital parentages.

In the present paper, we describe photophysical studies of several d⁸ square planar complexes of Pt(II) which reveal the presence of multiple emitting states. The specific complexes investigated are of the type Pt(diimine)(dithiolate) and are shown as 1–3.



	N-N	R	S-S
(1)	dmbpy	ethyl	ecda
(2)	dpphen	ethyl	ecda
(3)	dpphen	<i>t</i> -butyl	tbcdca

Complexes Pt(dmbpy)(ecda) (1), Pt(dpphen)(ecda) (2), and related analogues where dithiolate = 1-(ethoxycarbonyl)-1-cyanoethylene-2,2-dithiolate (ecda), 1,1-dicyanoethylene-2,2-dithiolate (*i*-mnt), and maleonitriledithiolate (mnt) and diimine = bipyridine (bpy), its 4,4'-dimethyl and -diphenyl derivatives (dmbpy and dpbpy respectively), *o*-phenanthroline (phen), and its 4,7-diphenyl derivative (dpphen) have been reported previously.^{5,6} The complexes are extraordinary in exhibiting luminescence in fluid solution, an extremely rare property for d⁸ square planar systems. In fact, prior to the report of Pt(dmbpy)(ecda) (1) and Pt(dpphen)(ecda) (2), only a handful of mononuclear Pt(II) complexes were known to emit in fluid solution,^{7–10} and of these, all but one had an excited state assigned as a $\pi-\pi^*$ intraligand state. The one case of a Pt(II) complex emitting in fluid solution from a state having metal orbital involvement was that of the cyclometalated species Pt(thpy)₂ (thpy = ortho-C-deprotonated form of 2-(2-thienyl)pyridine).⁷

The previously described complexes Pt(dmbpy)(ecda) (1) and Pt(dpphen)(ecda) (2) were observed to be highly solvatochromic in their absorption spectra and to undergo electron-transfer quenching with the electron donor *N,N*-dimethylaniline and the electron acceptor *o*-nitrobenzaldehyde.⁶ The present study focuses on elucidation of the excited states of these complexes. The emission spectroscopy of 1–3, including lifetimes and relative quantum yields, is examined as a function of solvent and temperature, and on the basis of these studies, the complexes are believed to possess multiple emitting states having different orbital parentages.

Experimental Section

Materials, Methods, and Preparations. The salt K₂PtCl₄ (Johnson-Matthey) was used as received without further purification. The potassium salts of 1-(ethoxycarbonyl)-1-cyanoethylene-2,2-dithiolate, K₂(ecda), and 1-(*tert*-butoxycarbonyl)-1-cyanoethylene-2,2-dithiolate, K₂(tbcdca), and the complexes Pt(dmbpy)Cl₂ and Pt(dpphen)Cl₂ were prepared according to literature procedures.^{11,12} Pt(dmbpy)(ecda) (1) and

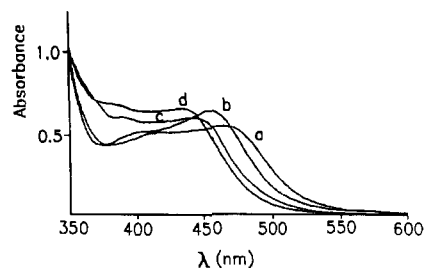


Figure 1. Room-temperature absorption spectra of Pt(dpphen)(ecda) (2) in (a) C₆H₆, (b) CH₂Cl₂, (c) acetone, and (d) MeCN.

Pt(dpphen)(ecda) (2) were synthesized as described previously,⁶ while Pt(dpphen)(tbcdca) (3) was synthesized by a completely analogous route. Syntheses were performed under N₂ using standard Schlenk and inert-atmosphere techniques. All solvents used were of spectral grade quality and were dried, distilled, and rigorously degassed before use.

Pt(dpphen)(tbcdca) (3). A 0.135-g (0.22-mmol) sample of Pt(dpphen)Cl₂ was dissolved in 20 mL of acetone. To the solution was added 0.073 g (0.25 mmol) of K₂(tbcdca) in 20 mL of methanol. The bright orange precipitate was separated by centrifugation, washed with water, methanol, and ether, and recrystallized from methylene chloride. The IR spectrum (KBr, cm⁻¹) shows peaks due to coordinated dpphen by comparison with the spectra of Pt(dpphen)Cl₂ (1626, 1561, 1030, 853, 766 cm⁻¹) and tbcdca (2199, 1447, 1138 cm⁻¹). ¹H NMR (CD₂Cl₂): δ 8.77 (d, 2 H), 8.21 (s, 2 H), 8.06 (d, 2 H), 7.62–7.95 (m, 10 H), 1.51 (s, 9 H). Anal. Calcd for PtC₃₀H₂₁N₃O₂S₂: C, 51.74; H, 3.39. Found: C, 51.96; H, 3.39.

Spectroscopic Characterization. Infrared spectra were obtained from KBr pellets on a Mattson Sirius 100 FTIR spectrophotometer. ¹H NMR spectra (400 MHz) were recorded on a Bruker AMX-400 spectrometer. Chemical shifts are referenced relative to the CHDCl₂ solvent resonance at δ 5.32 ppm. Absorption spectra were recorded on a Perkin-Elmer diode array UV-visible spectrophotometer interfaced to an IBM PC computer.

Solution emission measurements were performed on deoxygenated samples using a Spex Fluorolog fluorescence spectrophotometer. Low-temperature measurements were performed using a Janis liquid-helium cryostat equipped with Lake Shore Cryotronics DRC-82C temperature controller. Solution lifetimes were measured by single-photon counting, and low-temperature lifetimes were measured by transient digitization. The instrumental setups have been described elsewhere.⁶

Low-temperature emission spectra were recorded in DMM glasses (DMF/CH₂Cl₂/MeOH (1:1:1, v/v/v)) in which the samples were excited with the 442-nm line of a He–Cd laser. The emission signal was passed through a Corning 3-72 filter and a Cary monochromator with 0.2-mm slits and was detected with a Tektronix 762 photomultiplier tube. The signal was processed through a PAR 117 differential preamplifier and an EG&G 5208 two-phase lock-in amplifier. Spectra were recorded and integrations were performed using a Hewlett Packard 9122 computer. Relative quantum yields for the low-temperature samples were calculated using Ru(bpy)₃²⁺ as a standard ($\Phi = 0.38$ at 77 K in MeOH/EtOH).¹⁴ The fits of 1/ τ and Φ/τ vs 1/ T were obtained using ENZFIT, a nonlinear iterative program from Elsevier Biosoft.

Results

Complexes Pt(dmbpy)(ecda) (1) and Pt(dpphen)(ecda) (2) were prepared as previously described,⁶ while Pt(dpphen)(tbcdca) (3) was synthesized analogously from Pt(dpphen)Cl₂. Characterization of Pt(dpphen)(tbcdca) (3) was done by electronic, infrared, and ¹H NMR spectroscopies and elemental analysis.

Solvent Effects. The three diimine dithiolate complexes, Pt(dmbpy)(ecda) (1), Pt(dpphen)(ecda) (2), and Pt(dpphen)(tbcdca) (3), all exhibit an intense band in the 25 000–20 000-cm⁻¹ (400–500-nm) range of their respective room-temperature absorption spectra, which shows strong solvatochromism.⁶ This is illustrated in Figure 1 for Pt(dpphen)(ecda) (2). On the basis of detailed studies of the solvatochromism of these complexes and related analogues and molecular orbital calculations, this band is assigned as a metal/dithiolate-to-diimine charge-transfer transition and will be discussed in a separate paper.¹⁵

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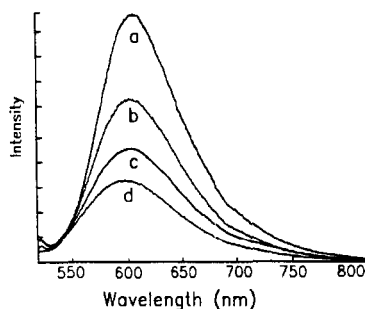


Figure 2. Relative emission intensity of Pt(dpphen)(ecda) (2) at room temperature in (a) C₆H₆, (b) CH₂Cl₂, (c) acetone, and (d) MeCN.

Table I. Relative Room-Temperature Quantum Yield Φ and Emission Lifetime τ of Pt(dpphen)(ecda) (2) as a Function of Solvent

solvent	Φ_{rel}	τ , ns	τ_0 , μ s
C ₆ H ₆	0.0140	125	8.9
CHCl ₃	0.0045	36	8.0
CH ₂ Cl ₂	0.0027	21.7	8.0
(CH ₃) ₂ CO	0.0024	18	7.5
CH ₃ CN	0.0017	11	6.5

The room-temperature emission spectra of 1–3 show a single broad and asymmetric band centered around 16 670 cm⁻¹ (600 nm) with no discernible vibronic structure. In marked contrast with their respective absorption spectra, the emission spectra of these complexes show only minimal shifts in position with solvent polarity. For example, the low-energy absorption band of Pt(dpphen)(ecda) (2) blue-shifts ~50–60 nm upon going from benzene to DMF, while a change of only ~10 nm is seen in the corresponding emission spectra.

While the room-temperature emission energy is unaffected by solvent polarity, the relative intensity of the 16 670-cm⁻¹ (600-nm) band decreases markedly as solvent polarity increases, as shown in Figure 2 for Pt(dpphen)(ecda) (2). Solutions of complexes 1–3 were prepared in solvents of different polarities ranging from benzene to DMSO, and relative quantum yields were determined using Ru(bpy)₃²⁺ in DMF ($\Phi = 0.042$) as a standard.¹³ For all of the samples, the solutions were absorbance-matched to the Ru(bpy)₃²⁺ in DMF standard at 22 935 cm⁻¹ (436 nm). The relative quantum yields for Pt(dpphen)(ecda) (2) at room temperature which are given in Table I illustrate the change in relative emission intensity with solvent polarity. For example, a solution of Pt(dpphen)(ecda) (2) in benzene, the least polar solvent used, exhibits a relative quantum yield of 1.4%, whereas in acetonitrile the value of Φ_{rel} is almost an order of magnitude lower. In very polar solvents such as DMF, the 16 670-cm⁻¹ (600-nm) emission band becomes very weak (less than 10% of the intensity observed in C₆H₆) and a different emission band is observed at ~20 410 cm⁻¹ (490 nm). In DMF, the intensity of this higher energy emission is slightly lower than that of the 600-nm band, while, in DMSO, the 600-nm emission disappears completely and only the higher energy band is observed.

Excitation spectra of 1–3 in fluid solution at ambient temperature were measured at λ_{em} 16 670 cm⁻¹ (600 nm) and were found to show a dependence on solvent polarity closely parallel to that of the absorption spectra, with the lowest energy excitation band shifting to higher energy as the solvent polarity increases.

Measurement of excited-state lifetimes in solution was performed for Pt(dpphen)(ecda) (2) in a series of solvents of increasing polarity by single-photon counting. In all cases, single-exponential decays were observed after deconvolution of the laser pulse. The solution lifetimes at 25 °C (Table I) follow the same trend observed for the relative quantum yields; i.e., the lifetimes decrease with increasing solvent polarity, from 125 ns in C₆H₆ to 11 ns in MeCN.

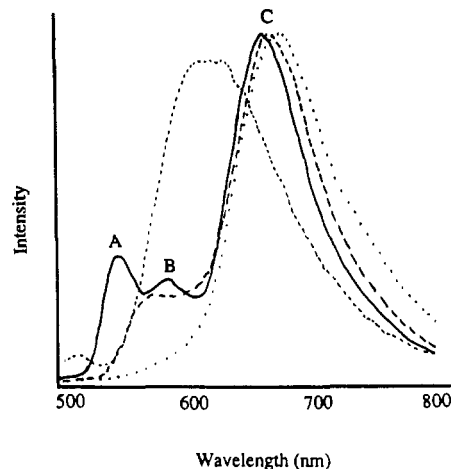


Figure 3. Emission spectrum of Pt(dpphen)(ecda) (2) in DMM at (---) 298 K, (---) 165 K, (---) 140 K, and (—) 80 K.

For the Pt(diimine)(dithiolate) complexes, the expressions for the lifetime τ and quantum yield Φ are given by eqs 1 and 2, respectively, where k_r and k_n represent the rate constants for radiative and nonradiative decay, respectively, from the excited state T₁ to ground state S₀ and Φ_{isc} is the quantum yield for intersystem crossing from the excited singlet states to T₁. If the excited-state lifetime τ is divided by the relative quantum yield Φ_{rel} in the same solvent, one obtains eq 3, and an experimental

$$\tau = \frac{1}{k_r + k_n} \quad (1)$$

$$\Phi = \frac{\Phi_{isc} k_r}{k_r + k_n} \quad (2)$$

$$\tau_0 = \frac{\tau}{\Phi} = \frac{1}{\Phi_{isc} k_r} \quad (3)$$

value of ~7.8 μ s which is essentially independent of solvent. This is seen in the data of Table I. The near constancy of τ_0 shows that $\Phi_{isc} k_r$ is invariant to solvent, which in turn means that the efficiency of intersystem crossing is solvent independent. If Φ_{isc} is essentially unity, as has been seen in a number of related complexes, then the natural radiative lifetime is equivalent to τ_0 . The fact that the relative quantum yield decreases with increasing solvent polarity is thus ascribable to increasing rates of nonradiative decay in more polar solvents.

The natural radiative lifetime, τ_0 , of ~7.8 μ s suggests that the emission from Pt(dpphen)(ecda) (2) is occurring from a triplet excited state although it must be noted that singlet and triplet designations have only limited significance in these complexes due to the large spin-orbit coupling of the Pt(II) ion.^{16,17} Nevertheless, the relatively long radiative lifetime indicates a certain degree of spin-forbidden character present in the excited state.

A concentration dependence study of the absorption and emission spectra of Pt(dpphen)(ecda) (2) in both acetone and CH₂Cl₂ shows that neither the energy nor the shape of the low-energy absorption band changes over the concentration range 10⁻⁶–10⁻³ M and that the emission and excitation bands also remain unchanged over the same concentration range. The absorption and excitation behavior indicate that the solvatochromic absorption band is due to a monomeric species, while the constancy of emission energy over 3 orders of magnitude in concentration rules out the possibility of excimer emission as has been reported for other Pt(diimine) complexes such as Pt(dpphen)(CN)₂.¹⁸

Temperature Effects. The emission spectra of Pt(dmbpy)(ecda) (1) and Pt(dpphen)(ecda) (2) were studied as a function of tem-

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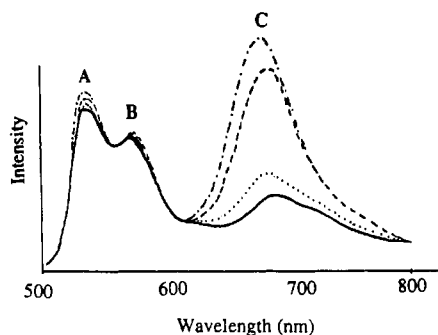


Figure 4. Emission spectrum of Pt(dpphen)(ecda) (2) in DMM at (---) 50 K, (---) 17 K, (---) 10 K, and (—) 6 K.

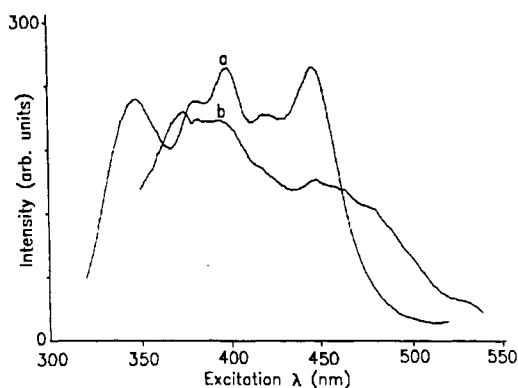


Figure 5. Excitation spectra of Pt(dpphen)(ecda) (2) collected at (a) 540 nm and (b) 670 nm at 16 K in DMM glass.

perature in DMF/CH₂Cl₂/MeOH (DMM) solution frozen glass. For Pt(dmbpy)(ecda) (1) and Pt(dpphen)(ecda) (2), emission quantum yields were determined between 6 and 50 K using Ru(bpy)₃Cl₂ in EtOH glass as a standard.¹⁴ From room-temperature to ~175 K, an increase in emission intensity is observed, while the emission energy and band shape remain constant. From 175 to 165 K, a sharp shift of 1540 cm⁻¹ to lower energy occurs, as shown for Pt(dpphen)(ecda) (2) in Figure 3. This temperature range corresponds to the glassing temperature of the solvent combination. Below 140 K, two new emission bands centered around 18 500 cm⁻¹ (540 nm) and separated by 1360 cm⁻¹ begin to emerge, and from 140 to 100 K, these bands (labeled A and B in Figure 3) as well as the lower energy band at 14 900 cm⁻¹ (670 nm) (labeled C) increase in intensity. At ~80 K, bands A and B reach a maximum in intensity, as measured by the quantum yield ($\Phi^{540} = 0.165$), and remain relatively constant upon further cooling of the sample down to 6 K. In contrast, band C shows a large decrease in emission intensity which is accompanied by a slight red shift as the temperature is lowered from 50 to 6 K. This is illustrated in Figure 4 for Pt(dpphen)(ecda) (2). Pt(dpphen)(tbcda) (3) exhibits almost identical behavior, with only a minor shift in the position of the bands. In the case of Pt(dmbpy)(ecda) (1), both bands A and B are blue-shifted by ~1300 cm⁻¹ with respect to those of Pt(dpphen)(ecda) (2) and are also slightly broader and less resolved than those of Pt(dpphen)(ecda) (2).

Different excitation spectra are obtained depending on the collection wavelength. This is shown in Figure 5 for Pt(dpphen)(ecda) (2). Collection at either A or B results in a more structured excitation spectrum with a very intense low-energy band at 22 400 cm⁻¹ (446 nm). In contrast, collecting at C yields an excitation spectrum which more closely resembles the absorption spectrum shown in Figure 1, with a low-energy shoulder centered near 20 000 cm⁻¹ (500 nm). The emission maxima are given in Table II. While the ratio of the relative intensities of bands A and B remains constant as the temperature is lowered, and is independent of the wavelength used for excitation, the ratio of band A (or B) to band C changes significantly with the excitation wavelength. For example, if the sample is excited at 500 nm rather

Table II. Emission Maxima for Pt(diimine)(dithiolate) Complexes in DMM Glass at 6 K

compd	emission band, 10 ³ cm ⁻¹ (nm)		
	A	B	C
Pt(dmbpy)(ecda) (1)	19.88 (503)	18.52 (540)	15.87 (630)
Pt(dpphen)(ecda) (2)	18.59 (537)	17.24 (580)	14.88 (672)
Pt(dpphen)(tbcda) (3)	18.60 (537)	17.39 (575)	14.77 (677)

Table III. Temperature Dependence of the Lifetimes of Band C in DMM Glass

temp, K	τ , μ s		τ , μ s	
	Pt-(dmbpy)-(ecda) (1)	Pt-(dpphen)-(ecda) (2)	Pt-(dmbpy)-(ecda) (1)	Pt-(dpphen)-(ecda) (2)
6.0	84	144	12.5	68
7.1	81	141	16.7	53
8.3	79	133	25.0	17
10.0	75	116	50.0	4.8

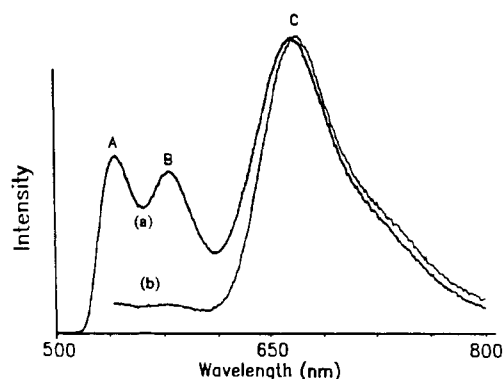


Figure 6. Emission spectra of Pt(dpphen)(ecda) (2) excited at (a) 440 nm and (b) 500 nm at 16 K in DMM glass.

than at 442 nm, only the low-energy band C is observed as seen in Figure 6. At the excitation wavelength λ_{ex} of 500 nm, the temperature dependence of the emission intensity of band C is the same as that observed with 442-nm excitation; that is, the relative intensity and hence quantum yield for emission decrease as the temperature is lowered. Bands A and B have previously been assigned to an intraligand (IL) $^3\pi-\pi^*$ diimine-based excited state, while band C has been tentatively attributed to a metal-dithiolate charge-transfer (MLCT) transition. These assignments are discussed further below.

Lifetime measurements for Pt(dmbpy)(ecda) (1) and Pt(dpphen)(ecda) (2) at temperatures down to 6 K were done in rigid DMM glass by transient digitization. Different values of τ were obtained depending on the wavelength used for monitoring the emission. Bands A and B were found to possess a single lifetime which was longer than that obtained for band C. For example, bands A and B of Pt(dpphen)(ecda) (2) decay with a lifetime of 500 μ s at 6 K, whereas band C decays with a lifetime of 144 μ s. A tabulation of lifetimes for band C as a function of temperature is given in Table III for Pt(dmbpy)(ecda) (1) and Pt(dpphen)(ecda) (2). As expected, lifetimes increase with decreasing temperature for both Pt(dmbpy)(ecda) (1) and Pt(dpphen)(ecda) (2), consistent with activated pathways for non-radiative decay.

Discussion

Analysis of Low-Temperature Emission Data. Between room temperature and 175 K, the only change in the emission spectra of the complexes is the relative intensity of the emission, which increases as the temperature is lowered. A sharp change in emission energy of ~1300 cm⁻¹ occurs between 175 and 165 K, coincident with glassing of the medium. This change corresponds to an effect termed rigidochromism, which has been observed previously in compounds of the type CpReL₃ (Cp = η^5 -cyclopentadienyl; L = CO, Cl, R) studied by Wrighton and Lees.^{19,20}

For the three complexes studied here, new bands A and B emerge in the emission spectra below 140 K and increase in intensity until 80 K (see Figure 3). Upon further cooling, the intensity of these bands remains relatively constant, while that of the CT band, band C, diminishes dramatically. These results suggest that bands A and B belong to the same excited state, which differs from that of band C. The excitation spectra of the complexes strongly support this conclusion. When the emission is monitored at either band A or B, the same excitation spectrum results, whereas when the emission is collected at 15 150 cm^{-1} (660 nm) (band C), a different excitation spectrum is obtained. Further corroboration is provided by the dependence of the emission on λ_{ex} . As seen in Figure 6, when Pt(dpphen)(ecda) (2) is excited at 442 nm, all three emission bands appear but when λ_{ex} of 500 nm is employed, only band C is observed in the emission.

The lifetime studies offer insight into the excited-state structure of these complexes. The identical and relatively long lifetimes of bands A and B, combined with the fact that these bands are separated by only 1360 cm^{-1} , strongly imply that bands A and B result from a ligand-based state and that the two bands correspond to vibronic components of the same excited state. Since emission of this type is well-known in phenanthroline- and bipyridine-containing complexes and has been attributed to $^3(\pi-\pi^*)$ states in the emission of Pt(5,5'-Me₂bpy)(CN)₂,²¹ M(bpy)₃ⁿ⁺ and M(phen)₃ⁿ⁺ complexes (M = Ir, Rh, Zn)²² and Zn(diimine)(RS)₂ (R = 2,3,5,6-tetramethylphenyl-2-chlorophenyl) complexes,²³ the assignment of bands A and B as due to a diimine intraligand $^3(\pi-\pi^*)$ state seems evident. The fact that this feature of the emission is identical for Pt(dpphen)(ecda) (2) and Pt(dpphen)(tbcda) (3) and slightly different for Pt(dmbpy)(ecda) (1) lends further support to the assignments. Additionally, the dichloride complex Pt(dpphen)Cl₂ exhibits emission in DMM glass at 77 K at 18 300 and 17 100 cm^{-1} (545 and 583 nm, respectively), corresponding to a separation of $\sim 1200 \text{ cm}^{-1}$.

The observation of different lifetimes for bands A (and B) and band C at low temperature indicates that they are not in thermal equilibrium below 100 K. Previously, band C has been ascribed to a charge-transfer state involving the dithiolate ligand on the basis of evidence that the emission changes dramatically in going from the Pt(diimine) complexes with the 1,2-dithiolate mnt to those with the 1,1-dithiolates ecda and tbcda used here.⁶ The lifetime measured for band C is also of the magnitude seen for charge-transfer states of third transition series elements in which a degree of spin forbiddenness exists in the excited state. A similar emission in Zn(diimine)(RS)₂ complexes (R = 2,3,5,6-tetramethylphenyl-2-chlorophenyl) was ascribed to a thiol-to-diimine ligand-to-ligand charge transfer (LLCT).^{23b-d} A detailed analysis of the nature of the emitting state for 1-3 based on systematic ligand variation and molecular orbital calculations, which will be presented separately,¹⁵ leads to the conclusion that for these 1,1-dithiolate complexes the emission corresponding to band C comes from a {(metal-d/sulfur-p)- π^* (diimine)} excited state.

An extraordinary feature of the emission and lifetime data for band C is that while the lifetime gets longer as the temperature is lowered (as expected), the quantum yield for emission does not increase concomitantly. In fact, the emission quantum yield for band C decreases with decreasing temperature, as shown by Figure 4. These observations cannot be accommodated by a model for

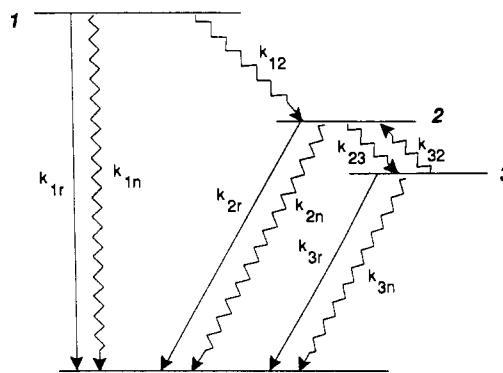


Figure 7. Excited-state manifold of the Pt(diimine)(ecda) complexes where 1-3 refer to different excited states.

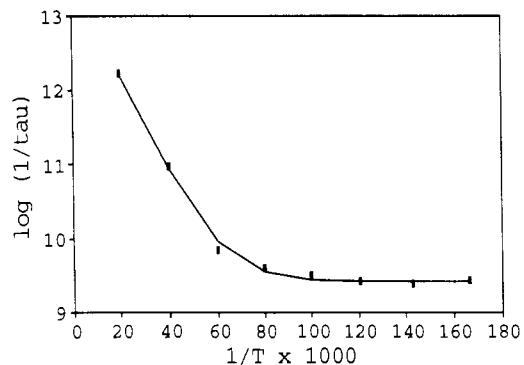


Figure 8. Computer-generated fit of $\ln(1/\tau)$ vs $1/T$ for Pt(dpphen)(ecda) (2).

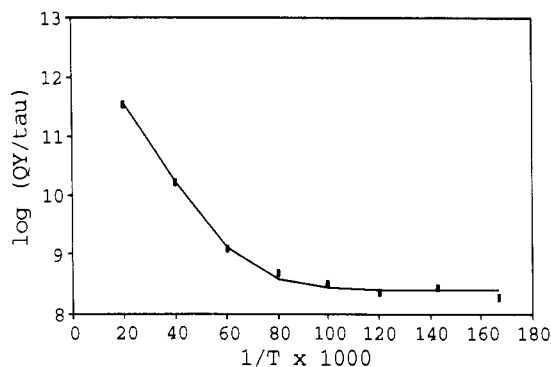


Figure 9. Computer-generated fit of $\ln(\Phi/\tau)$ vs $1/T$ for Pt(dpphen)(ecda) (2).

band C of a single emitting state. For a single-state model, the temperature dependence of the lifetime and the quantum yield for emission would change in the same direction. This may be understood from the same denominators in eqs 1 and 2 for τ and Φ and from the notion that radiationless decay k_n is composed of a temperature-independent path and temperature-dependent activated processes of an Arrhenius type. This model has been used by Barigelletti et al. to analyze the temperature dependence of τ for Pt(thpy)₂.²⁴ The present results, however, are inconsistent with this model and require the presence of two or more thermally equilibrated excited states for satisfactory analysis.

The excited-state structure and kinetic model employed in our analysis is shown in Figure 7, in which the two states labeled 2 and 3 yield the emission observed as band C. The $^3(\pi-\pi^*)$ state responsible for bands A and B discussed above is also included in Figure 7 and is labeled as 1. Above 120 K, all three states appear to be in thermal equilibrium on the basis of the single emission observed which decays as a single exponential, giving one lifetime. Below 100 K, state 1 is no longer thermally

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equilibrated with states 2 and 3. The latter are spin-orbit-split components of a ³CT state which remain in thermal equilibrium down to 30 K. This is supported by the single-exponential decay observed in the lifetime measurements of band C. The expressions for the lifetime and quantum yield obtained from the model in Figure 7 are shown in eqs 4 and 5 where $k_3 = k_{3r} + k_{3n}$ and $k_2 = k_{2r} + k_{2n}$.

$$\tau = \frac{1 + e^{-\Delta E/kT}}{k_3 + k_2 e^{-\Delta E/kT}} \quad (4)$$

$$\Phi = \frac{k_{3r} + k_{2r} e^{-\Delta E/kT}}{k_3 + k_2 e^{-\Delta E/kT}} \quad (5)$$

The temperature-dependent lifetime and quantum yield data for Pt(dpphen)(ecda) (2) are plotted as $\ln(1/\tau)$ and $\ln(\Phi/\tau)$ versus $1/T$ in Figures 8 and 9, respectively, in which the solid lines correspond to computer-generated fits based on eqs 4 and 5. The values for the energy separation (ΔE) and the rate constants (k_{in} and k_{ir}) are given in Table IV.

Proposals of thermally equilibrated excited states have been made previously for systems including d⁶ diimine complexes such as Ru(bpy)₃²⁺²⁵ and for CpRe(CO)₂L,² Cu(phen)(PPh₃)₂²⁺,²⁶ M(2=phos)₂ClO₄,¹⁷ and M(diene)(diimine)⁺ (M = Rh, Ir)²⁷ to rationalize lifetime and emission quantum yield data. The basis of the splitting which leads to states 2 and 3 in the present study appears to be spin-orbit coupling. A group theoretical analysis was proposed by Gliemann et al. for Pt(diimine)(CN)₂ complexes,^{28,29} including both electron interaction and spin-orbit coupling. Our proposal appears to be consistent with this model.³⁰ The value of ΔE is ~ 60 cm⁻¹, which is within the expected range

Table IV. Computer-Fit Rate Constants and Energy Separation for Pt(dmbpy)(ecda) (1) and Pt(dpphen)(ecda) (2)

	Pt(dmbpy)(ecda) (1)	Pt(dpphen)(ecda) (2)
k_{2r} , s ⁻¹	6.16×10^5	9.95×10^5
k_{2n} , s ⁻¹	5.46×10^5	12.80×10^5
k_{3r} , s ⁻¹	4.39×10^3	1.73×10^3
k_{3n} , s ⁻¹	7.86×10^3	5.72×10^3
ΔE , cm ⁻¹	54.2	52.5

for the splitting of spin-orbit states for a third-row d⁸ metal center,^{17,27} and the values of k_{2r} and k_{3r} for both Pt(dmbpy)(ecda) (1) and Pt(dpphen)(ecda) (2) are consistent with radiative rate constants for spin-orbit states of third-row transition metal complexes. In contrast, the radiative rate constant k_r ⁵⁴⁰ for bands A and B is calculated from Φ^{540}/τ^{540} to be 3.2×10^3 s⁻¹ ($\tau_0 = 3$ ms), which is in accord with the assignment of A and B as a ³($\pi-\pi^*$) diimine-based state.³¹

Conclusions

From the study of the solvent dependence of the luminescence spectra and lifetimes of Pt(diimine)(dithiolate) complexes 1-3, it is found that both the emission quantum yield and lifetime decrease as a function of solvent polarity. This is explained by the ability of polar solvents to promote nonradiative decay of the excited state. From the temperature dependence of the emission spectra and lifetimes of Pt(dmbpy)(ecda) (1) and Pt(dpphen)(ecda) (2), a model is proposed involving three emitting states. The two lowest energy states are spin-orbit components of a ³CT state with an energy separation of $\sim 50-60$ cm⁻¹. The highest energy emitting state corresponds to a ³($\pi-\pi^*$) diimine-based transition. While not observed above 120 K, this state is not thermally equilibrated with the other two below ~ 100 K, at which temperature it emerges in the emission spectra of the complexes.

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Registry No. 1, 123623-04-1; 2, 123623-05-2; 3, 139348-48-4; Pt(dpphen)Cl₂, 35273-41-7; K₂(tbcda), 139348-49-5; C₆H₆, 71-43-2; CHCl₃, 67-66-3; CH₂Cl₂, 75-09-2; (CH₃)₂CO, 67-64-1; CH₃CN, 75-05-8.

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- (30) While only two spin-orbit split states are required in our model, Gliemann has shown that spin-orbit coupling in analogous Pt(diimine)(CN)₂ systems results in four possible states, ¹B₁(B₁') and ³B₁(A₁' + A₂' + B₂'). Of the three states originating from the triplet, only two (A₁' and B₂') are dipole allowed, thus giving a total of three emitting states (B₁', A₁' and B₂'). However, A₁' and B₂' are accidentally degenerate even in single crystals and at temperatures as low as 1.9 K. Emission from the third triplet component, A₂', is only vibronically allowed and was only observed as a weak band below 5 K.²⁸ Thus, the higher energy emission originates from the B₁' state and the lower energy band arises from the degenerate A₁' and B₂' states.

- (31) The effect of spin-orbit coupling in transitions that involve the metal atom directly is expected to be much greater than in a transition involving perturbed ligand orbitals.