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PLATINUM(II) DIIMINE DITHIOLATES. NEW SOLUTION LUMINESCENT COMPLEXES

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SUMMARY

A series of Pt(diimine)(dithiolate) complexes has been synthesized and characterized spectroscopically. The diimine ligands include 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 4,4′-dimethyl-2,2′-bipyridine (dmbpy), 4,4′-diphenyl-2,2′-bipyridine (dpbpy) and 4,7-diphenyl-1,10-phenanthroline (dpphen) while the dithiolates are maleonitriledithiolate (mnt), 2,2-dicyano-1,1-ethylenedithiolate (i-mnt) and ethyl-2-cyano-3,3-dithiolatoacrylate (ecda). The complexes are solvatochromic showing a linear correlation of absorbance with solvent polarity. The most notable feature of the complexes is that they luminesce in fluid solution. The luminescence differs depending on the nature of the dithiolate - mnt complexes show structured emissions while i-mnt and ecda complexes do not - but the emitting state appears to be d-π^*(dithiolate) for all complexes. The relative quantum yields for emission have been determined, as have lifetime measurements at 298 K and 77 K in both rigid and fluid media. Quenching studies have been done for Pt(dpphen)(mnt) and Pt(dpphen)(ecda) using dimethylaniline (DMA) as a donor and o-nitrobenzaldehyde (ONB) as an acceptor. Good Stern-Volmer behavior is observed for both reductive and oxidative quenching.

INTRODUCTION

Square planar complexes are among the earliest studied transition metal luminophores. Most of the attention in this regard has focused on complexes of Pt(II) such as PtX_4^{2-} (X = Cl, CN), $Pt(N\text{-}N)_2^{2+}$ (N-N = bpy, phen, diimine) and $Pt(N\text{-}N)X_2$, and has involved luminescence in the solid state or in rigid media at low temperature.[1-4] The earliest studies of the PtX_4^{2-} systems have been reviewed.[1] In more recent work, Webb, et al.,[2] have observed luminescence for the platinum diimine complexes $Pt(N\text{-}N)Cl_2$ but no emission maxima, structural information, quantum yields or lifetimes were reported. For a series of charged and neutral Pt(II) complexes, Camassei studied the effect of counter ion and molecular geometry on emission spectra, and found longer emission lifetimes for trans isomers over cis and for those complexes with ligand π systems.[3] In none of these reports were the Pt complexes observed to be solution luminescent.

Other square planar complexes have also been found to be luminescent in the solid state. These systems include a number of Rh(I) and Ir(I) complexes

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with chelating di(phosphine) and diimine ligands, and the emitting states in these systems have been ascribed to MLCT transitions.[5-7] In 1983 Eisenberg, et al., reported the synthesis and characterization of a series of luminescent square planar complexes of general formula $[MLL'(mnt)]^{n-}$ (n = 1, M = Rh, Ir; n = 0, M = Pt; L, L' = CO, PR_3, $P(OR)_3$; mnt = maleonitriledithiolate).[8] These complexes exhibited highly structured emission and excitation spectra in the solid state and in frozen solution. The similarity of the vibronic structure among the Ir, Rh and Pt complexes, together with shifts in the emission maxima as a function of electron donating ability of L and L', supported assignment of a common emitting state as MLCT involving the dithiolate ligand. Since measured lifetimes were on the order of 10^{-6} sec with samples exhibiting single exponential decays, the emitting state of these complexes was designated as $^3(d\text{-}\pi_{mnt})$.

Luminescence from d^8 complexes in fluid solution is a relative rarity. One set of d^8 complexes which do emit are binuclear systems exemplified by $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ and $Rh_2(1,3\text{-diisocyanopropane})_4^{2+}$.[9] For mononuclear complexes of square planar geometry, the absence of luminescence in fluid solution arises because of efficient radiationless decay via collisions with solvent in the open coordination sites of the square plane. For the few mononuclear Pt(II) complexes that do emit in fluid solution, the state responsible for the emission has been assigned in most cases to a π-π* intraligand state.[10-11] To date the only reported case of a Pt(II) complex that emits in solution from a state showing metal involvement is that of the cyclometallated species $Pt(thpy)_2$ (thpy = 2,2'-thiophenylatopyridine).[12]

In the present study, a new series of platinum complexes containing a diimine and a dithiolate has been prepared having the general formula Pt(N-N)(S-S). Prior to this work, only a few complexes of this type had been reported[13,14] with one example showing evidence of luminescence. Unlike the phosphine and carbonyl mnt complexes, these new systems exhibit intense absorption in the visible region of the spectrum and luminesce detectably both in the solid state and in fluid solution at room temperature. These new complexes are also found to undergo electron transfer quenching with donor and acceptor molecules, opening up the possibility of utilizing these systems as photocatalysts.

EXPERIMENTAL

Materials and Methods

The reagents K_2PtCl_4 (Johnson-Matthey), 2,2'-bipyridine (bpy), 1,10-phenantroline (phen), 4,4'dimethyl-2,2'-bipyridine (dmbpy), 4,4'diphenyl-2,2'-bipyridine (dpbpy) and 4,7-diphenyl-1,10-phenanthroline (dpphen) (Aldrich) were used as received without further purification. All solvents were of spectral grade quality and, except where noted, were dried and distilled before use.

Drying agents are specified in parentheses for the following solvents: acetonitrile and benzonitrile (P_2O_5); benzene and THF (sodium-benzophenone ketyl); acetone, DMF, DMSO, choroform and methylene choride ($CaSO_4$). Cyclohexanone, chlorobenzene and 1,2-dichloroethylene were used as received. For luminescence measurements, solvents were distilled under vacuum and degassed using 3 freeze-pump-thaw cycles. The compounds Pt(bpy)Cl_2, Pt(phen)Cl_2, Na_2(mnt), K_2(i-mnt) and K_2(ecda) were prepared according to literature methods;[15-19] other PtLCl_2 compounds where L= dmbpy, dpbpy and dpphen were prepared by analogous procedures. Syntheses were performed under N_2 using standard Schlenk and inert atmosphere techniques. Yields of Pt(diimine)(dithiolate) complexes were typically 50-80%.

Pt(bpy)(mnt), **1a**. 0.106 g (0.25 mmol) of Pt(bpy)Cl_2 was dissolved in 40 mL of hot acetonitrile to which was added 0.047 g (0.25 mmol) of Na_2(mnt) in 10 mL acetonitrile. A red precipitate formed which was collected by filtration, washed with acetonitrile and acetone, and vacuum dried. The IR spectrum (KBr, cm^{-1}) contains peaks assignable to coordinated bpy by comparison with a spectrum of Pt(bpy)Cl_2 and to mnt: 2203 (s, C≡N), 1471 (s, C=C) and 1157 (m).

Pt(phen)(mnt), **1b**. This complex was prepared by an analogous procedure using 0.111 g of Pt(phen)Cl_2 and 0.047 g of Na_2(mnt). The yellow-orange solid obtained was filtered and washed with acetonitrile and acetone. The IR spectrum (KBr, cm^{-1}) contains peaks due to coordinated phen by comparison with a spectrum of Pt(phen)Cl_2 and to mnt: 2206 (s, C≡N) and 1496 (s, C=C). Anal. Calcd. for $PtC_{16}H_8N_4S_2$: C, 37.28; H, 1.56; N, 10.87; S, 12.43. Found C, 37.24; H, 1.36; N, 10.74; S, 12.17.

Pt(dmbpy)(mnt), **1c**. 0.083 g (0.15 mmol) of Pt(dmbpy)Cl_2 was dissolved in 20 mL of DMSO and 0.054g (0.3 mmol) of Na_2(mnt) in 5 mL of methanol was added. The mixture was stirred for 10 min upon which a red-orange precipitate formed which was filtered and washed with water, ethanol and ether. The IR spectrum (KBr, cm^{-1}) contains peaks due to coordinated dmbpy by comparison with a spectrum of Pt(dmbpy)Cl_2 and to mnt: 2201 (s, C≡N) and 1447 (s, C=C), 1155 (m). ^{1}H NMR (CD_2Cl_2): δ 8.84 (d, 2H), 7.92 (s, 2H), 7.41 (d, 2H), 2.54 (s, 6H)

Pt(dpbpy)(mnt), **1d**. 0.143g (0.25mmol) of Pt(dpbpy)Cl_2 was dissolved in 30 mL of degassed THF and 0.05 g of Na_2(mnt) in MeOH was added. The solution was stirred at room temperature for 2 hr during which time the solution became red. Upon addition of 20 mL of water, a dark red precipitate formed which was collected by centrifugation. More precipitate formed after the supernatant liquid was evaporated to ~20 mL. Both precipitates were washed 3 times with ethanol/acetone (1:1 v/v) and ether, and were found to be spectroscopically identical. IR (KBr, cm^{-1}): 2205 (s, C≡N), 1495 (s, C=C), and 1157 (m); ^{1}H NMR (CD_2Cl_2): δ 9.06 (d), 8.40 (s), 7.83 (d), 7.63 (s).

Pt(dpphen)(mnt), **1e**. This complex was prepared by an analogous procedure to that for Pt(bpy)(mnt) using 0.148 g of Pt(dpphen)Cl_2. The IR spectrum (KBr, cm^{-1}) contains peaks due to coordinated dpphen by comparison with a spectrum of Pt(dpphen)Cl_2 and peaks assignable to mnt: 2206 (s, C≡N) and 1496 (s, C=C). ^1H NMR (CD_2Cl_2): δ 9.35 (d, 2H), 8.10 (s, 2H), 7.89 (d), 7.64 (s).

Pt(bpy)(i-mnt), **2a.** 0.083 g of Pt(bpy)Cl_2 was dissolved in 30 mL of hot acetone to which was added 0.70 g of K_2(i-mnt) in 10 mL of methanol. The bright orange-red precipitate was collected by centrifugation, washed with acetone, ethanol and ether, and vacuum dried. IR (KBr, cm^{-1}): 2207 (s, C≡N), 1431 (s, C=C), 1160 (m).

Pt(phen)(i-mnt), **2b.** This complex was prepared using a procedure analogous to that used for Pt(dmbpy)(mnt) using 0.10 g of Pt(phen)Cl_2 and 0.08 g of K_2(i-mnt). The resulting red solution was refrigerated for 8 h during which time a yellow precipitate formed. The precipitate was separated by centrifugation and washed with acetone, ethanol and ether. IR (KBr, cm^{-1}): 2209 (s, C≡N) and 1451 (s, C=C), 1145 (m).

Pt(dmbpy)(i-mnt), **2c.** 0.125 g (3.7 mmol) of Pt(dmbpy)Cl_2 was dissolved in 30 mL of acetone to which was added 0.8 g of K_2(i-mnt) in 10 mL of methanol. The bright orange precipitate was separated by centrifugation, washed with acetone, ethanol and ether, and vacuum dried. IR (KBr, cm^{-1}): 2207 (s, C≡N) and 1487 (s, C=C).

Pt(dpbpy)(i-mnt), **2d.** This tan yellow complex was prepared in the same manner as the mnt analog **1d**. IR (KBr, cm^{-1}): 2207 (s, C≡N) and 1472 (s, C=C), 1157 (m).

Pt(dpphen)(i-mnt), **2e**. This tan-orange complex was prepared in the same manner as the mnt analog **1e**. IR (KBr, cm^{-1}): 2205 (s, C≡N) and 1476 (s, C=C), 1157 (m). ^1H NMR (CD_2Cl_2): δ 9.91 (d, 2H), 8.10 (s, 2H), 7.89 (d, 2H), 7.64 (s, 10H, C_6H_5). Anal. Calcd. for $PtC_{28}H_{16}N_4S_2$: C, 50.37; H, 2.42; N, 8.30; Found C, 49.29; H, 2.18; N, 7.90.

Pt(dmbpy)(ecda), **3c.** This complex was obtained by a procedure identical to that used for Pt(dmbpy)(i-mnt), **2c**. The red precipitate obtained was washed with methanol and acetone and recrystallized from methylene chloride as a yellow powder. IR (KBr, cm^{-1}) shows peaks due to coordinated dmbpy by comparison with Pt(dmbpy)Cl_2 and to ecda: 2203, 1449 and 1153. ^1H NMR (CD_2Cl_2): δ 8.31 (d, 1H), 8.21 (d, 1H), 7.92 (s, 2H), 7.37 (d, 2H), 4.22 (q, 5.5Hz, 2H), 2.59 (s, 6H), 1.33 (t, 5.5 Hz, 3H). Mass spectrum: parent peak at m/e 566. Anal. Calcd. for $PtC_{18}H_{17}N_3O_2S_2$: C, 38.16; H, 3.02; N, 7.42; Found C, 37.82; H, 2.89; N, 6.90.

Pt(dpphen)(ecda), **3e.** This complex was prepared by an identical procedure to that used for Pt(dmbpy)(ecda), **3c**. The orange powder was washed with methanol and ether and recrystallized from methylene chloride. ^1H NMR (CD_2Cl_2): δ 8.65 (d, 1H), 8.57 (d, 1H), 8.08 (s, 2H), 7.77-7.65 (m, 12H), 4.09 (q, 2H), 1.23 (t, 3H). Anal. Calcd. for $PtC_{30}H_{21}N_3O_2S_2$: C, 50.42; H, 2.96; N, 5.88; Found C, 50.01; H, 2.84; N, 5.60.

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 WH-400 spectrometer. Chemical shifts are reported downfield from internal solvent peaks (CD_2Cl_2, δ_H=5.32; acetone-d_6, δ_H=2.04). Absorption spectra were recorded on a Perkin-Elmer diode array UV-visible spectrophotometer interfaced to an IBM PC computer. Solid state luminescence measurements were recorded on a Perkin Elmer MPF-44A Fluorimeter. Samples were prepared by smearing a small amount of the compound on a glass microscope slide and covering it with a plastic slide cover. The luminescence was measured using the front surface and was maximized by manually aligning the sample. Fluid solution luminescence measurements were performed on a Spex Fluorolog fluorescence spectrophotometer. A quartz dewar with flat windows was used for the low temperature measurements. Temperature was lowered by adding the appropriate solvent/coolant combination to the devar. Relative quantum yields were measured on the same equipment used for solution luminescence measurements with $[Ru(bpy)_3]Cl_2$ employed as the emission standard. Emission curves were corrected for phototube response and the formula

$$\Phi_{sample} = \frac{I_{sample} \times \Phi_{std} \times A_{std}}{I_{std} \times A_{sample}}$$

was used where I_{sample} and I_{std} are the integrated emission intensities and A_{sample} and A_{std} are the absorbances at the excitation wavelength of the sample and the standard, respectively.

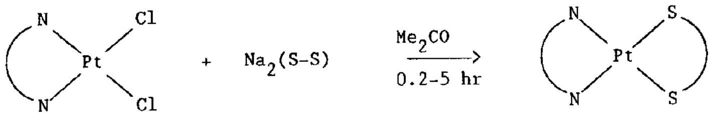
Lifetimes in the solid state were measured by exciting the sample with a PRA Nitromite N_2 laser pumping on stilbene 420. System response was adjusted to 0.15 μs for mnt complexes and ~4 ns for i-mnt and ecda. The signal was filtered though a Corning 3-73 glass cutoff filter and American ISA Monochromator with 0.5 μm slits, was detected with a RCA 931C photomultiplier tube at 1200V, and was analyzed with a Tektronix 7912AD programmable digitizer with 7A16p or 7A22 amplifier vertical plug and 71390p horizontal plug. Data analysis was performed on an IBM 9000 series computer. A least squares routine was used to fit the lifetimes for single exponential decays and a simple deconvolution technique was used to resolve the components of double exponential decay after which lifetimes were fitted with the same least squares routine.

Solution lifetimes were determined using a time correlated single photon counter with a Nd-YAG Quantronics 116 pumping laser operating at 8 watts and 76 MHz to produce 100 ps pulses. The 1064 nm YAG output was frequency doubled using a KTP crystal and the 532 nm radiation was used to excite a Coherent 700 cavity dumped dye laser producing 80 ps pulses of 594 nm radiation. The 1064 nm radiation and the dye output were mixed in a $LiIO_3$ crystal to obtain 381 nm radiation used to excite the sample. The emission was passed through a Spex 1681 monochromator and collected on a PR TE271RF multichannel plate photomultiplier tube, amplified using a Bertran 315 amplifier and an EG&G time-to-amplitude converter. The resulting data were processed on an IBM PC using a multiple exponential fit routine to minimize χ^2 and distribute the residuals uniformly along the axis.

Electrochemical measurements were done in degassed benzonitrile or DMF using a Princeton Applied Research 173 potentiostat and 175 PAR sweep generator and a Houston 200 xy recorder. Cyclic voltammograms were measured using a single-compartment three electrode cell containing a glassy-carbon electrode, a platinum gauze auxiliary electrode and a Ag/AgCl reference electrode. $(TBA)PF_6$ (0.1M) was used as the supporting electrolyte. All oxidation and reduction waves are reported vs NHE using the ferrocene/ferrocenium couple (0.4 V) as an internal standard.

RESULTS AND DISCUSSION

All of the Pt complexes described here are readily prepared by the reaction of the dichlorodiimine complex $Pt(N-N)Cl_2$ in acetone, DMSO or acetonitrile with an excess of the dithiolate ligand as shown in eq. 1.



(1)

	N-N	S-S
1a	bpy	mnt
1b	phen	mnt
1c	dmbpy	mnt
1d	dpbpy	mnt
1e	dpphen	mnt
2a	bpy	i-mnt
2b	phen	i-mnt
2c	dmbpy	i-mnt
2d	dpbpy	i-mnt
2e	dpphen	i-mnt
3c	dmbpy	ecda
3e	dpphen	ecda

bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline
dmbpy = 4,4′-dimethyl-2,2′bipyridine
dpbpy = 4,4′-diphenyl-2,2′bipyridine
dpphen =4,7-diphenyl-1,10-phenanthroline
mnt = maleonitriledithiolate = 1,2-dicyano-1,2-ethylenedithiolate
i-mnt = 2,2-dicyano-1,1-ethylenedithiolate
ecda = ethyl-2-cyano-3,3-di(thiolato)acrylate

Characterization was done by electronic, infrared and ^{1}H NMR spectroscopies, field desorption mass spectrometry, and in several cases, by elemental analyses. The spectroscopic data show the compounds to be mononuclear square planar complexes of the formula Pt(N-N)(S-S) where (N-N) is a diimine and (S-S) is a dithiolate ligand. Compound 3c shows two crystalline forms depending on the solvent of crystallization; a red form from acetone and a yellow form from methylene chloride. The conversion between these two forms is completely reversible by recrystallization, and they show identical solution spectra and the same parent ion peak in the mass spectrum at m/e 566. However, the two forms of 3c exhibit significant differences in their solid state emission and excitation spectra (vide infra). The two forms of 3c are undoubtedly related to solid state structural effects as has been seen for red and yellow $Pt(bpy)Cl_2$ in which the red form possesses a stacked structure in the solid.

Unlike the starting compounds of formula $Pt(N\text{-}N)Cl_2$, the diimine dithiolate complexes exhibit an intense absorption in the visible region of the spectrum with molar extinction coefficients in the range of 12,000-16,000 $M^{-1}cm^{-1}$. For each diimine ligand, the transition for the mnt complex occurs at lower energy than those of the i-mnt and ecda analogs. In all cases, the absorption is broad (average width at half maximum of ~3500-4000 cm^{-1}) and highly solvatochromic. Due to the low solubility of the complexes containing mnt and i-mnt in most common solvents, a complete study of the solvatochromic behavior was possible only for the ecda derivatives and for one of the mnt systems. For these complexes, there exists an excellent correlation between the observed transition energy and the E^*_{MLCT} solvent polarity scale developed by Lees.[20] This is illustrated in Figure 1. Dong's Py solvent scale[21] also gave good correlation with the observed transition energies, but other solvent

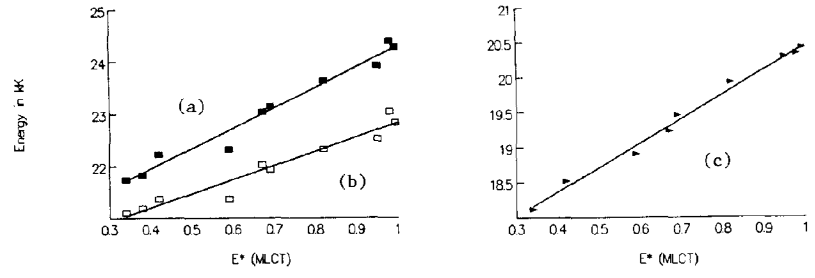


Figure 1. Correlation between transition energy and E*$_{MLCT}$ for (a) Pt(dmbpy)(ecda), (b) Pt(dpphen)(ecda) and (c) Pt(dpphen)(mnt).

polarity scales - solvent dielectric constant, Kosower's Z scale,[22] and Reichhardt's ET(30)[23] - yielded much poorer agreement.

The successful correlation of the absorption band energy with Lees' E^*_{MLCT} scale and the lack of correlation with the other solvent scales can be understood based on the facts that: (1) dielectric constant is a bulk property of the solvent and does not reflect accurately the behavior within the solvation shell; (2) both the Z and ET(30) scales are based on compounds that show a high degree of hydrogen bonding, a property absent in the present series of complexes; and (3) the Lees' E^*_{MLCT} scale uses as its basis electronic transitions similar to those observed here.

All of the compounds of formula Pt(N-N)(S-S) luminesce detectably at room temperature in the solid state. For a given dithiolate, a change in the diimine ligand leads only to a shift in the energy and a small change in the intensity of the emission. In contrast, changing the dithiolate ligand leads to completely different emissive behavior. The difference is particularly noticeable upon changing from the 1,2-dithiolate (mnt) to the 1,1-dithiolates (i-mnt and ecda). The compounds containing mnt as the dithiolate show weak but structured luminescence at 298 K. At lower temperatures, there is a gradual increase in intensity with a sharpening of the structure, but the position of the emission maximum remains unchanged in going from 298 to 77 K. The vibrational structure appears remarkably similar to that reported previously for the phosphine and carbonyl mnt complexes for which a metal-to-ligand d-π^*_{mnt} excited state has been assigned.[8] Although the emission maxima are less resolved in some of the Pt compounds, a vibronic progression of 1300-1400 cm^{-1} can be assigned. This is illustrated in Figure 2 with the emission and excitation spectra of Pt(dmbpy)(mnt), **1c**. For the mnt complexes, the intensity

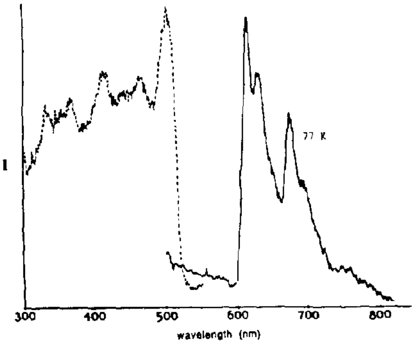


Figure 2. Excitation (---) and emission (——) spectra of Pt(dmbpy)(mnt), **1c**, in the solid state at 77 K.

of the luminescence and the emission maxima vary with the nitrogen donor, being weakest for Pt(bpy)(mnt) and strongest for Pt(dmbpy)(mnt).

The i-mnt and ecda compounds show a more intense but unstructured luminescence at room temperature in the solid state. At lower temperatures, there is a small increase in intensity, although proportionately much smaller than that observed for the mnt analogs, and there is no appreciable structure even at 77 K. However, the emission maximum shifts to lower energies by ~10-30 nm when cooled from 298 to 196 K, followed by a further 10-30 nm shift upon cooling to 77 K. Figure 3 shows the temperature dependence of the emission maximum for Pt(dmbpy)(i-mnt), 2c. For the red and yellow forms of 3c, different λ_{em}'s are seen which shift to longer wavelengths at 77 K, as illustrated in Fig. 4. Absorption, emission and excitation maxima of the different complexes are listed in Table I.

All of the compounds tested show luminescence in solution at room temperature. In all cases, the luminescence maximum is blue shifted by 1000-1500 cm^{-1} relative to the solid state samples. In contrast with the absorption spectra, there is little solvent dependence of the energy of the emission bands, but the intensity of the emission increases with decreasing solvent polarity. All of the mnt complexes show some structure even at room temperature. For the i-mnt and ecda compounds, the emissions are broad and asymmetric without discernible vibronic structure. This is illustrated in Fig. 5 for the dpphen derivatives 1e and 3e. These observations regarding solution emission structure are consistent with the solid state emission spectra of these compounds.

TABLE I

Energies of the Absorption, Emission and Excitation Maxima for the Pt(diimine)(dithiolate) Complexes[a]

Compound	E_{abs}	E_{em}	E_{exc}
1a	20.00*	16.05 (15.87)	19.08
1b	19.60*	15.87 (16.00)	17.79
1c	21.19*	16.26 (16.13)	20.08
1d	19.49	14.64	15.38
1e	19.03	14.83	15.77
2a		14.70 (15.87)	-
2b	23.64*	15.80	-
2c	23.98(20.66sh)	14.70 (15.87)	-
2d	22.30	14.64	20.40
2e	22.52	15.38	19.23
3c	20.33	13.89 (15.15)	16.95
		15.65 (16.18)	20.83
3e	20.33	15.24 (15.24)	19.61

[a] All values are reported in cm^{-1} x 10^{3}. Absorption spectra were measured in methylene chloride or benzonitrile solution (marked *). Emission and excitation values are from data at 77 K; values in parentheses are at 298 K.

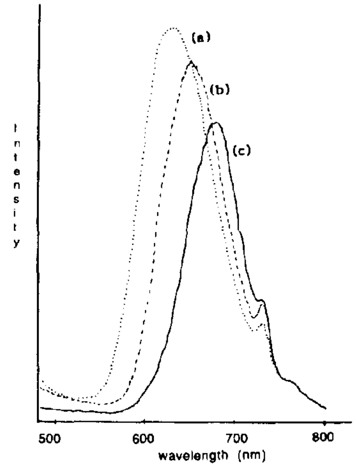


Figure 3. Solid state emission spectra of 2c at (a) 298 K, (b) 196 K and (c) 77 K. Intensity scale is not the same for all spectra.

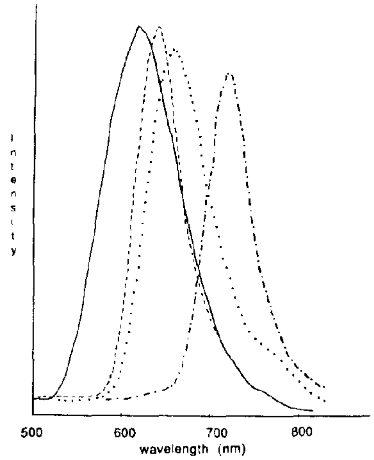


Figure 4. Emission spectra of 3c in the solid state: yellow form, 298 K(——) and 77 K (---); and red form at 298 K (·····) and 77 K (–·–·).

A more detailed temperature study of the emission of 3e in CH_2Cl_2/DMF/MeOH shows a shift to lower energy upon cooling to a glass and the emergence of new bands at higher energy below 90 K attributable to a dpphen-based π-π^* excited state (Figure 6). The excitation spectrum of 3e differs with λ_{em} used for collection; at 540 and 580 nm it appears characteristic of the dpphen π-π^* state,[24] but at 660 nm it is broad and less structured (Fig. 6).

Excitation spectra of both the mnt and i-mnt cases show large Stokes shifts (~2000-4000 cm^{-1}), indicative of distorted excited state geometries. The

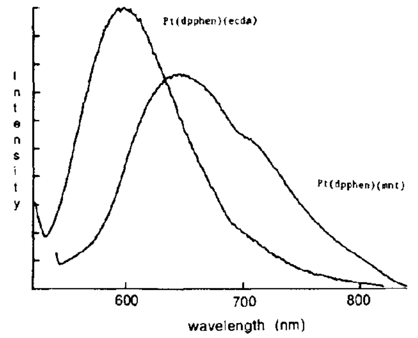


Figure 5. Solution emission spectra of 1e and 3e in CH_2Cl_2 at 298 K.

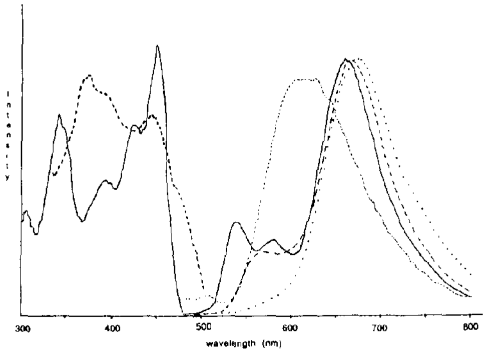


Figure 6. (a) Excitation spectra of Pt(dpphen)(ecad), **3e**, at 77 K in DMF/CH_2CL_2/MeOH collected at 540 nm (——) and 640 nm (- - -). (b) Emission spectra at 80 K(——), 140 K(- - -), 165 K(·····) and 210 K(-·--).

low resolution of the excitation spectra of the i-mnt and ecda complexes makes difficult the assignment of vibronic progression. For the mnt complexes, however, a vibronic progression of ~1200 cm^{-1} can be discerned (Figure 2) which agrees with those seen for the carbonyl and phosphine mnt complexes reported previously. The similarity in the absorption and excitation spectra within each series of complexes is indicative of a common electronic transition for all the compounds containing a common dithiolate.

The nature of the excited states in these complexes has not been unambiguously determined, nor has it been established whether the excited states of complexes containing different dithiolate ligands have in fact the same orbital parentage. For the mnt complexes, the similarity of the vibronic progressions with those of the previously reported carbonyl and P-donor analogs strongly suggests a similar emitting state involving a $d\text{-}\pi^*_{mnt}$ MLCT transition. For the i-mnt and ecda complexes, the lack of vibrational structure makes more difficult the excited state assignment, and necessitates consideration of other possible transitions.

A literature survey reveals that for d^8 square planar complexes of Ir and Rh containing bpy as a ligand, solid state emissions were observed at 77 K which showed a vibronic progression characteristic of the diimine ligand.[7] The excited state was thus assigned as a MLCT involving the diimine ligand. For a series of Ni(N-N)(S-S) complexes, interligand $\pi\text{-}\pi^*$ transitions were assigned in the absorption spectra of these systems based on electrochemical and spectroscopic data for related bis diimine and bis dithiolate complexes.[25] The same assignment of $\pi\text{-}\pi^*$ states was extrapolated for the low energy absorption and emission of Pt(BABA)(tdt) and Pt(BABA)(mnt) (BABA=biacetil-bis-anil, tdt=3,4 toluenedithiolate).[13a] Recently, a LF transition was proposed for the solid state emission of Pt(N-N)Cl_2 complexes which are closely related to the systems under consideration here.[26]

At this point, despite the differences in the emissions of the mnt and 1,1-dithiolate complexes, we favor for the latter a MLCT state involving the dithiolate ligand based on the following considerations: (1) the similarity of the emission within a series of complexes containing a common dithiolate; (2) the marked differences in emission characteristics between 1,1- and 1,2-dithiolate complexes, even for the same diimine ligand; (3) the fact that no emission is observed for Pd and Ni i-mnt and ecda analogs, providing evidence against intra- or interligand excited states;[27] (4) the fact that Pt(N-N)Cl_2 complexes do not show a strong absorption band in the visible spectrum as is seen for the corresponding dithiolate complexes and that they emit only as solids at low temperature even though chloride is similar in ligand field strength to dithiolates;[28] (5) the excellent correlation which is observed between absorption energy for 3c, 3e and 1c and Lees' E^*_{MLCT} solvent scale; and (6) the photochemical behavior of the complexes including the observation of electron transfer quenching (vide infra).

The multiple lifetimes found for the 1,1-dithiolate complexes and the temperature dependence of their emission maxima suggest the possibility of more than one emitting state for these systems as seen for 3e (Fig. 6). Multiple state luminescence has been reported for a number of metal complexes,[29] but in only one case are complexes of dithiolate ligands involved.[29h] In most of the reported cases, the excited states are thermally equilibrated and expressions have been derived by Crosby for emission quantum yield, lifetime and relative intensity for a given state as a function of temperature.[2] A few cases of non-equilibrated multiple state luminescence have been reported recently,[29a] and this possibility must also be considered for the present series of complexes.

Relative quantum yields for solution emission were measured using $[Ru(bpy)_3]^{2+}$ in DMF as a standard (Φ_{em} = 0.068).[30] Measurements were done in rigorously dried, distilled and degassed solvents. In all solvents, the relative quantum yields followed the trend ecda > mnt > i-mnt. The values of Φ_{em} vary with solvent polarity and show good correlation with the E^*_{MLCT} scale. In mixtures of CH_2Cl_2 and DMF, the quantum yield varies as a function of the solvent ratio. Table II lists the relative emission quantum yields in three solvents.

Emission lifetimes in the solid state range from 13 ns to 1 μs at room temperature and from 0.9 to 12 μs at 77 K. The complexes containing mnt show a single exponential decay whereas the i-mnt and ecda complexes exhibit double exponential decays with a short-lived component that is predominant at shorter wavelength, and a long-lived component predominant at longer wavelength. Deconvolution results in two single exponential decays. The lifetimes at 298 K

TABLE II

Compound	Relative quantum yield (x 10^4)		
	DMF	Acetone	CH_2Cl_2
1a	1.9		
1b	-		
1c	1.5		
1d	8.3		5.8
1e	6.7		4.1
2a			
2b			
2c	0.5		
2d	1.9		
2e	3.1		
3c	1.4	1.6	2.7
3e	13.3	19.5	26.9

and 77 K including the deconvoluted values are presented in Tables III. The two components in the emission of the i-mnt series with lifetimes which differ by factors of 2 to 30 give further evidence for the notion of multiple emitting states in these systems. The magnitude of the lifetimes at 77 K suggests that in all cases a significant degree of spin forbiddenness is involved in the emitting state transitions, although for the i-mnt complexes the higher energy component appears to have more singlet character. However, due to the large spin-orbit coupling constant for Pt(II), the labeling of singlet and triplet states has only relative significance.

TABLE III

Emission Lifetimes of Platinum Diimine Dithiolate Complexes

Compound	τ (298 K)	τ (77 K)
1a	1040	6100
1b	670	2000
1c	600	-
1d	89	-
1d	11.2^a	-
1e	130	-
1e	25.3^a	-
2b	-	190, 800
2c	40, 150	400, 800
2d	18, 86	-
2e	20, 300	600, 22000
3c(Y)	16, 109	630, 1740
3c(R)	12, 78	436, 1390
3c	13.5, 3.4^a	3100^b
3e	7, 26	407, 2200
3e	21.2^a	1800^b

[a] Measured in CH_2Cl_2 solution. [b] Measured in DMF/CH_2Cl_2/MeOH glass.

The Pt(N-N)(S-S) complexes were also examined electrochemically. From cyclic voltammograms, $E_{1/2}$ values were determined for reversible reductions and E_p values were measured for irreversible oxidation and reduction waves. The trend observed for the reduction waves is the same in both the mnt and i-mnt series. The oxidation wave, however, is constant within a common dithiolate for the bpy, phen, and dmbpy complexes but appears at less positive potentials for the complexes containing phenyl substituted diimines. The c.v.'s for **3c** and **3e** are shown in Figure 7.

TABLE IV

Electrochemical Data for Platinum Diimine Dithiolate Complexes

Compound	$E_{1/2}^{red(1)}$	$E_{1/2}^{red(2)}$	E_p^{ox}
1a	-1.21	-1.73	1.06
1b	-1.23	-1.70	1.07
1c	-1.29	-1.78	1.07
1d	-1.18	-1.68	0.70
1e	-1.15	-1.72	0.72
2a	-1.21	-1.75	1.15
2b	-1.22	-1.73	1.15
2c	-1.28	-1.83	1.16
2d	-1.11	-1.71	0.72
2e	-1.18	-1.73	0.75
3c	-1.28	-1.77	0.83
3e	-1.12	-1.68	0.75

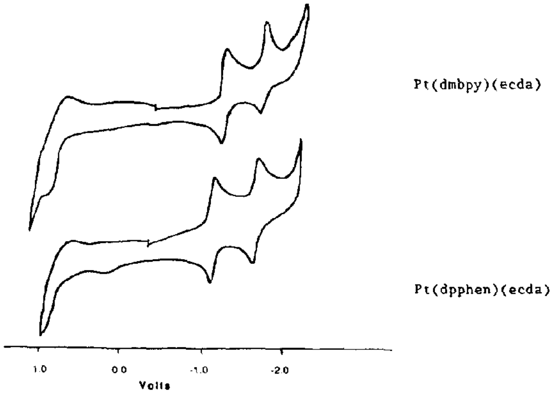


Figure 7. Cyclic voltammograms of (a) Pt(dmbpy)(ecda), **3c**, and (b) Pt(dpphen)(ecda), **3e**.

Quenching studies of 3e in CH_2Cl_2 have been performed using the electron donor N,N-dimethylaniline (DMA) and the electron acceptor o-nitrobenzaldehyde (ONB). From the Stern-Volmer plots such as is shown in Fig. 8, K_{SV} was determined to be 24.8 for ONB and 188 and for DMA. The corresponding k_q values calculated from K_{SV} and the solution excited state lifetime of 3e are 6.8×10^8 and 9×10^9 M^{-1} s^{-1}, respectively. Since the triplet energies of both ONB (61 kcal/mole)[31] and DMA (74 kcal/mole)[32] are significantly larger than that estimated for 3e from its emission (52 kcal/mole), the quenching was determined to be occuring via electron transfer. As is shown in Figure 9, irradiation of 3e in the presence of DMA (1.6×10^{-2} M) yields no change in absorption spectrum after 24 h whereas in a sample containing ONB (1.1×10^{-2} M), there is bleaching of the 454 nm band over 5 h indicating degradation of the complex by irreversible oxidation. This is consistent with the reversible reduction and irreversible oxidation of 3e in the cyclic voltammogram.

The quenching of Pt(dpphen)(mnt), 1e, in CH_2Cl_2 was also studied using o-nitrobenzaldehyde (ONB) and N,N-dimethylaniline (DMA). The energy of the excited state of 1e is 45 kcal/mole, which is again substantially less than the lowest triplet energies of DMA and ONB. As with 3e, good Stern-Volmer plots were obtained with $[1e] = 1 \times 10^{-5}$ M and quencher concentrations in the range 0.01 - 0.08 M. The Stern-Volmer constants determined from the plots were 11.2 and 25.6 for DMA and ONB, respectively, with calculated k_q values of 4.57×10^8 and 1.1×10^9 M^{-1} s^{-1}.

When quenching studies of 3e were performed using methylviologen (MV^{2+}) as the acceptor in DMF, good Stern-Volmer plots were not obtained. However, after irradiation of the samples with $\lambda > 350$ nm for 6 h, the occurrence of electron transfer was observed by disappearance of the band at 497 nm due to the starting complex 3e and appearance of a band at 387 nm corresponding to MV^+. The intensity of the 387 nm band and the decrease in the 497 band are functions of the concentration of MV^{2+} and are absent in a control sample containing no quencher.

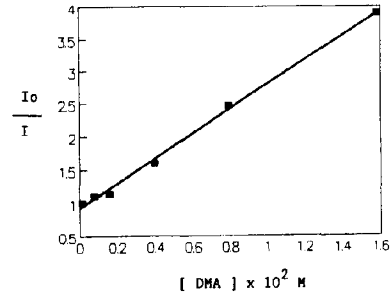


Figure 8. Stern-Volmer plot of Pt(dpphen)(ecda) with DMA.

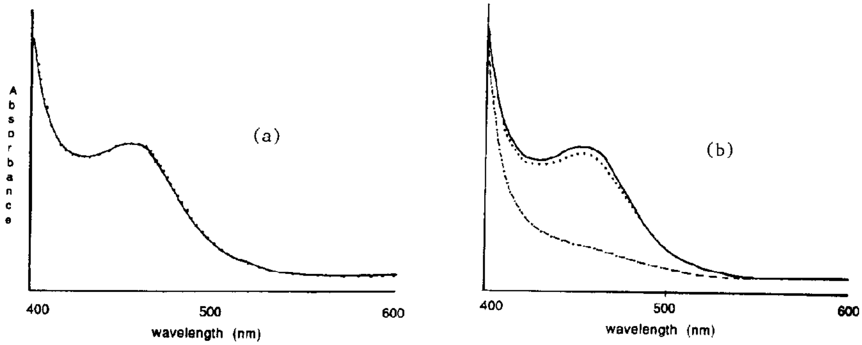


Figure 9. Absorption spectrum of Pt(dpphen)(ecda), **3e**, after photolysis in the presence of (a) DMA and (b) ONB.

CONCLUSIONS

A novel class of luminescent Pt(II) complexes has been prepared. The most distinctive features of these compounds are their fluid solution luminescence, their solvatochromic absorption spectra, and the emission thermochromism and dual lifetimes of the i-mnt and ecda series. The photochemical and photophysical properties of the compounds suggest most strongly that the emitting states are of the MLCT $d-\pi^*$(dithiolate) type, although the possibility of an interligand transition cannot be uneqivocally eliminated at this point. Selected members of the series undergo electron transfer quenching. Unlike $Ru(bpy)_3^{2+}$ and its d^6 analogs, the compounds described here are coordinatively unsaturated, making them good candidates as both photoreceptors and catalysts for light driven redox chemistry. Their low-lying CT spectra and electron transfer behavior suggest that these systems may have significant potential for use in the reduction of H^+ and CO_2. Studies oriented in this direction are underway.

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