

Synthesis and Characterization of Luminescent Square-Planar Platinum(II) Complexes Containing Dithiolate or Dithiocarbamate Ligands

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The synthesis, characterization, and emission properties of a series of Pt(L₂)(S-S) complexes are reported. The (L₂) ligands include 4,7-diphenyl-1,10-phenanthroline (Ph₂phen), 4,4'-dimethyl-2,2'-bipyridine (Me₂bpy), 1,5-cyclooctadiene (COD), trimethyl phosphite (P(OMe)₃), and the α-C-deprotonated form of 2-phenylpyridine (2-phpy). The (S-S) ligands include 1-(*tert*-butoxycarbonyl)-1-cyanoethylene-2,2-dithiolate (tbcda), 1-(diethoxyphosphinyl)-1-cyanoethylene-2,2-dithiolate (cpdt), *cis*-1,2-dicarbomethoxyethylene-1,2-dithiolate (met), and *N,N*-diethyldithiocarbamate (Et₂dtc). The complexes are readily synthesized by the addition of the dithiolate or thiolate ligand to Pt(L₂)Cl₂ except for Pt(P(OMe)₃)₂(met), which is prepared by the addition of 2 equiv of trimethyl phosphite to Pt(COD)(met). On the basis of characterizations using NMR and infrared spectroscopies, all of the complexes are assigned square-planar coordination geometries with varying degrees of distortion determined by ligand steric and electronic effects. The assignment of square-planar coordination is confirmed by single-crystal structure determinations of Pt(Me₂bpy)(met) (5) and Pt(P(OMe)₃)₂(met) (7). Purple crystals of Pt(Me₂bpy)(met)·CHCl₃ (C₁₉H₁₉Cl₃N₂O₄PtS₂) are monoclinic, of space group P2₁/n (No. 14), with *a* = 11.402(1) Å, *b* = 9.085(8) Å, *c* = 23.041(2) Å, β = 97.83(5)°, *V* = 2364.70 Å³, *Z* = 4, and final *R* = 0.024 (*R*_w = 0.030) for 3123 unique reflections. Pale yellow crystals of Pt(P(OMe)₃)₂(met) (7) (C₁₂H₂₄O₁₀P₂PtS₂) are monoclinic, of space group P2₁/c (No. 14), with *a* = 11.209(3) Å, *b* = 12.250(7) Å, *c* = 16.558(4) Å, β = 102.97(3)°, *V* = 2215.80 Å³, *Z* = 4, and final *R* = 0.047 (*R*_w = 0.061) for 4092 unique reflections. The average Pt–S distance of 5 is shorter than that of 7, being 2.244(7) and 2.301(4) Å, respectively. The average Pt–N distance of 2.055(1) Å for 5 and the average Pt–P distance of 2.238(9) Å for 7 agree well with previously reported structural results. The met chelate ring indicate some degree of metal–ligand delocalization in both structures. All of the complexes containing α,α'-diimine ligands are solvatochromic and exhibit strong luminescence in solution at room temperature. In particular, the complexes containing 1,1-dithiolates, Pt(Ph₂phen)(tbcda) (1) and Pt(Ph₂phen)(cpdt) (2), have a single featureless emission band in solution at room temperature at ~600 nm. Upon cooling of the samples to 77 K, two new higher energy bands emerge at 535 and 578 nm for 1 and 2 while the emission band at ~600 nm shifts to lower energy, ~650 nm. The emission and excitation spectra at 77 K are dependent upon the excitation wavelength. The cationic complex [Pt(Me₂bpy)(Et₂dtc)]PF₆ (3) exhibits similar emissive properties at room temperature with an emission band at 590 nm and at 77 K with two higher energy bands at 474 and 506 nm and a lower energy band at 564 nm. The Pt(2-phpy)(Et₂dtc) (4) complex is solution luminescent with a highly structured emission spectrum at both room temperature and 77 K. In contrast to those of the complexes containing 1,1-dithiolates, the emission and excitation spectra of Pt(Me₂bpy)(met) (5) do not vary with excitation wavelength. Also, the emission spectrum of 5 is structured with a vibrational progression of 1175 cm⁻¹. Pt(COD)(met) (6) and Pt(P(OMe)₃)₂(met) (7) exhibit strong emission in the solid state and in frozen glasses at 77 K with less resolved vibrational structure than is seen for complex 5.

Introduction

Square-planar complexes have been known for many years to have emissive excited states. The phenomenon of luminescence in these systems, however, was generally restricted to low temperatures (77 K or lower) and rigid media (glasses or solids). Examples include simple MX₄ complexes such as PtCl₄²⁻ and Pt(CN)₄²⁻,^{1,2} heteroaromatic chelates such as Pt(bpy)Cl₂³ and bis(diphosphine) chelates of Rh(I) and Ir(I).^{4–6} In 1983, we reported a series of luminescent anionic complexes of Rh(I) and Ir(I) having the general formula [MLL'(mnt)]ⁿ⁻ (L, L' = CO, PR₃, P(OR)₃ and mnt = maleonitriledithiolate) that were emissive at ambient temperatures but, again, only in rigid media.⁷ In all of the systems containing the 1,2-dithiolate mnt, the emission

was highly structured, and the shift in λ_{em} with donor ability of L and L' led to assignment of a common emitting state as a ³(d-π*_{mnt}) metal-to-ligand charge transfer.

The observation of square-planar Pt(II) complexes that emit in fluid solution is relatively recent,^{8–10} and the number of Pt(II) complexes with this property is relatively small.^{8–15} Poor solution emission may be caused by low-lying ligand field (dd) states that facilitate nonradiative decay^{13,15} or by open coordination sites

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that provide a pathway for radiationless relaxation via solvent interactions. It is interesting that the solution-emissive complexes that have been reported over the last 7 years by von Zelewsky, Balzani, Scandola, Vogler, Che, and Rillema all contain heteroaromatic ligands such as bpy, phen, and their alkylated derivatives or the isoelectronic α -C-deprotonated analogues such as the anions of 2-phenylpyridine and 2-(2-thienyl)pyridine.⁸⁻¹⁵ In most of the complexes, the emissive state has been assigned as a $^3(\pi-\pi^*)$ intraligand (IL) state, but for a few complexes, a metal-to-ligand charge-transfer (MLCT) state has been proposed.^{10,16}

In 1989, we reported a series of Pt(diimine)(dithiolate) complexes, related to the MLL' (mnt)-complexes described above, that were found to be solution emissive as well as highly solvatochromic.^{17,18} Complexes of two dithiolate ligands, maleonitriledithiolate (mnt) and 1-(ethoxycarbonyl)-1-cyanoethylene-2,2-dithiolate (ecda), have been investigated in detail. The main findings of these studies are (1) both the mnt and ecda complexes possess a solvent-dependent absorption band that is assigned to a charge-transfer band of (Pt(d)/S(p)- π^* diimine) character, (2) the ecda complexes possess multiple emitting states including a $^3(\pi-\pi^*)$ intraligand state of the diimine ligand and spin-orbit split components of a triplet state having the same orbital parentage as the solvatochromic transition, and (3) the mnt complexes have a single emitting state that is assigned as a $^3(\text{Pt}(\text{d})/\text{S}(\text{p})-\pi^*_{\text{mnt}})$ charge transfer.¹⁷⁻²¹

To probe further the electronic structure of emissive Pt(diimine)(dithiolate) complexes, we have undertaken the characterization of a series of related emissive platinum complexes containing dithiolate and dithiocarbamate chelates. The present study describes the synthesis and characterization of these systems as well as single-crystal X-ray structure determinations of two of these complexes. Complexes containing a diimine with either a dithiolate or a dithiocarbamate chelate exhibit a solvatochromic absorption band and are luminescent in solution at room temperature, while complexes containing 1,5-cyclooctadiene or trimethyl phosphite are luminescent only at 77 K.

Experimental Section

Materials, Methods, and Preparations. The reagents, K_2PtCl_4 (Johnson-Matthey), 4,4'-dimethyl-2,2'-bipyridine (Me_2bpy), 4,7-diphenyl-1,10-phenanthroline (Ph_2phen), 1,5-cyclooctadiene (COD), trimethyl phosphite ($\text{P}(\text{OMe})_3$), sodium hexafluorophosphate, 2-phenylpyridine (2-phpy), dimethyl acetylenedicarboxylate, ethylene trithiocarbonate, mercuric acetate, lithium methoxide (Aldrich), and sodium diethyldithiocarbamate ($\text{Na}(\text{Et}_2\text{dtc})$) (Eastman), were used as received without further purification. The potassium salts of 1-(*tert*-butoxycarbonyl)-1-cyanoethylene-2,2-dithiolate, $\text{K}_2(\text{tboda})$, and 1-(diethoxyphosphinyl)-1-cyanoethylene-2,2-dithiolate, $\text{K}_2(\text{cpdt})$,²² and the complexes $\text{Pt}(\text{Ph}_2\text{phen})\text{Cl}_2$, $\text{Pt}(\text{Me}_2\text{bpy})\text{Cl}_2$,²³ $\text{Pt}(\text{COD})\text{Cl}_2$,²⁴ and $\text{Pt}(\text{Ph}_2\text{phen})(\text{tboda})$ (1)²⁵ have been described previously. The ortho-metalated complex $\text{TBA}[\text{Pt}(\text{2-phpy})\text{Cl}_2]$, where 2-phpy is the α -C-deprotonated form of 2-phenylpyridine, was prepared according to the literature procedure.²⁶ Syntheses were performed under N_2 using standard Schlenk

and inert-atmosphere techniques. All solvents were of spectral grade quality and were dried, distilled, and degassed before use.

Pt(Ph_2phen)(cpdt) (2). A 0.135-g (0.22-mmol) sample of $\text{Pt}(\text{Ph}_2\text{phen})\text{Cl}_2$ was dissolved in 20 mL of acetone, and the solution was placed in an ice bath. To this was added 0.822 g (0.25 mmol) of $\text{K}_2(\text{cpdt})$ in 20 mL of methanol. The bright orange precipitate was separated from the mixture by centrifugation, washed with water, methanol, and ether, and recrystallized from methylene chloride. IR (KBr, cm^{-1}): 2980 and 2922 (w, C—H), 2187 (s, CN), 1445 (s, C=C), 1234 (s, C—S), 1024 (s, P=O). ^1H NMR (acetone- d_6): δ 8.62 (m, 2 H), 8.21 (s, 2 H), 8.02 (m, 4 H), 7.91 (m, 4 H), 7.64 (m, 4 H), 4.06 (m, 4 H), 1.26 (t, 6 H). ^{31}P NMR (acetone- d_6): δ 12.59.

[Pt(Me_2bpy)(Et_2dtc)]PF₆ (3). A 0.134-g (0.298-mmol) sample of $\text{Pt}(\text{Me}_2\text{bpy})\text{Cl}_2$ was placed in a 250-mL round-bottom flask wrapped in aluminum foil and suspended in 50 mL of distilled water. To the aqueous suspension was added with constant stirring 6 mL of 0.1 M AgNO_3 (0.6 mmol). The solution was heated to 45 °C for 6 h followed by stirring at room temperature for 16 h. The clear solution was filtered, and the filtrate was mixed with 0.070 g (0.31 mmol) of sodium diethyldithiocarbamate. After the solution was heated to 45 °C for 30 h, 0.051 g (0.30 mmol) of sodium hexafluorophosphate dissolved in 30 mL of distilled water was added. A yellow precipitate formed immediately and was collected by centrifugation. The precipitate was recrystallized from methylene chloride containing CaH_2 to remove any residual water, filtered off, and chromatographed on silica gel. The solvent volume was reduced to 10 mL, after which addition of 20 mL of ether resulted in the precipitation of a bright yellow powder that was collected, dried with ether, and stored under vacuum. IR (KBr, cm^{-1}): 2940 (w, C—H), 1549 (m, C—N), 1446 (w, C—N), 1283 (w, C—S). ^1H NMR (acetone- d_6): δ 8.590 (s, 2 H), 8.495 (d, 2 H, $^2J_{\text{H-H}} = 6$ Hz), 7.716 (d, 2 H, $^2J_{\text{H-H}} = 6$ Hz), 3.846 (q, 4 H, $^2J_{\text{H-H}} = 7$ Hz), 2.621 (s, 6 H), 1.412 (t, 6 H, $^2J_{\text{H-H}} = 7$ Hz). Anal. Calcd for $\text{PtC}_{17}\text{H}_{22}\text{F}_6\text{N}_3\text{PS}_2$: C, 30.36; H, 3.30; N, 6.25. Found: C, 30.25; H, 3.34; N, 6.45.

Pt(2-phpy)(Et_2dtc) (4). A solution of 0.432 g (0.191 mmol) of sodium diethyldithiocarbamate in 20 mL of methanol was added to 0.125 g (0.190 mmol) of $\text{TBA}[\text{Pt}(\text{2-phpy})\text{Cl}_2]$ in 50 mL of methylene chloride, and the solution was heated to 40 °C until it became yellow. The solvent volume was reduced to 5 mL, and 10 mL of ether was added. The resulting yellow-brown precipitate was dissolved in methylene chloride, and the solution was chromatographed on a silica gel column. Three bands separated with methylene chloride as eluent: a yellow band, then a green band, followed by an orange band. The yellow band was collected and the solvent volume reduced to 10 mL. Addition of 20 mL of ether resulted in the precipitation of a bright yellow powder, which was collected by centrifugation, dried with ether, and stored under vacuum. ^1H NMR (acetone- d_6): δ 8.597 (d with Pt satellites, 1 H, $J_{\text{H-H}} = 6$ Hz, $J_{\text{Pt-H}} = 19$ Hz), 8.082 (dt, 1 H, $J_{\text{H-H}} = 8$ Hz, $J_{\text{H-H}} = 2$ Hz), 8.010 (d, 1 H, $J_{\text{H-H}} = 8$ Hz), 7.680 (dd, 1 H, $J_{\text{H-H}} = 8$ Hz, $J_{\text{H-H}} = 2$ Hz), 7.31–7.27 (m, 1 H), 7.147 (dd, 1 H, $J_{\text{H-H}} = 8$ Hz, $J_{\text{H-H}} = 2$ Hz), 7.10–7.03 (m, 2 H), 3.825 (q, 2 H, $J_{\text{H-H}} = 7$ Hz), 3.784 (q, 2 H, $J_{\text{H-H}} = 7$ Hz), 1.359 (t, 3 H, $J_{\text{H-H}} = 7$ Hz), 1.331 (t, 3 H, $J_{\text{H-H}} = 7$ Hz). ^{13}C NMR (CDCl_3): δ 208.56 ($J_{\text{Pt-C}} = 51.95$ Hz), 166.47 ($J_{\text{Pt-C}} = 47.05$ Hz), 150.06 ($J_{\text{Pt-C}} = 13.26$ Hz), 146.18 ($J_{\text{Pt-C}} = 515.78$ Hz), 144.79 ($J_{\text{Pt-C}} = 23.62$ Hz), 137.76, 133.03 ($J_{\text{Pt-C}} = 44.50$ Hz), 130.41 ($J_{\text{Pt-C}} = 31.79$ Hz), 123.65 ($J_{\text{Pt-C}} = 18.89$ Hz), 123.10, 122.55 ($J_{\text{Pt-C}} = 18.35$), 118.87 ($J_{\text{Pt-C}} = 19.07$ Hz), 45.85, 44.64, 12.44.

4,5-Dicarbomethoxy-1,3-dithiol-2-one. This compound is the precursor to the lithium salt of *cis*-1,2-dicarbomethoxyethylenedithiolate (Li_2met) and is prepared according to the method of Brown *et al.*²⁷ with minor modifications as outlined below. A neat solution of 2.2 g (15 mmol) of dimethyl acetylenedicarboxylate was added to 2.03 g (15 mmol) of ethylene trithiocarbonate, and the mixture was heated to 135 °C for 15 min. The solution was cooled to 50 °C, and 30 mL of acetone was added. After 12 h, an additional 20 mL of acetone was added, resulting in immediate precipitation of an orange solid. Addition of 20 mL of pentane caused further precipitation. The orange precipitate, 4,5-dicarbomethoxy-1,3-dithiole-2-thione, was filtered off and placed in a vacuum desiccator overnight. The following day, 5 mL of a THF/methanol (1:1 v/v) solution was added to 0.125 g (0.50 mmol) of 4,5-dicarbomethoxy-1,3-dithiole-2-thione and 0.198 g (0.62 mmol) of mercuric acetate. This mixture was allowed to stir overnight until a black precipitate formed. The solution

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was filtered, yielding a slightly yellow filtrate containing 4,5-dicarbomethoxy-1,3-dithiol-2-one (0.50 mmol).

Pt(Me₂bpy)(met) (5). A 250-mL three-neck round-bottom flask was fitted with a condenser in the central neck and dropping addition funnel in a side neck. The round-bottom flask contained a suspension of 0.205 g (0.46 mmol) of Pt(Me₂bpy)Cl₂ in 40 mL of acetone, and the dropping addition funnel contained 0.044 g (1.16 mmol) of LiOMe dissolved in 10 mL of methanol. The round-bottom flask was heated to 50 °C, and the yellow filtrate containing 4,5-dicarbomethoxy-1,3-dithiol-2-one was added to the LiOMe solution. This solution was then added dropwise to the warm Pt(Me₂bpy)Cl₂ suspension, resulting in a red solution. After 2 h, the solution was cooled to room temperature.

The solvent volume was reduced to 20 mL and the red-brown precipitate filtered off and washed with 20 mL of H₂O/methanol (1:1 v/v) solution to remove any unreacted salts. The precipitate was dissolved in a minimum amount of methylene chloride, and the solution was chromatographed through an alumina column. A 2% solution of methanol in methylene chloride was used to elute a purple band, which was set aside. Increasing amounts of methanol also eluted an uncharacterized orange band. The purple solution was reduced to 20 mL, and ether was added to cause formation of a red precipitate. The red precipitate was collected by centrifugation, dried with ether, and stored under vacuum. IR (KBr, cm⁻¹): 2945 (w, C—H), 1722 and 1693 (s, C=O), 1530 (s), 1431 (s, C=C), 1234 (s). ¹H NMR (CDCl₃): δ 8.616 (d, 2 H, ²J_{H-H} = 6 Hz), 7.761 (s, 2 H), 7.098 (d, 2 H, ²J_{H-H} = 6 Hz), 3.814 (s, 6 H), 2.422 (s, 6 H). Anal. Calcd for PtC₁₈H₁₈N₂O₄S₂: C, 36.92; H, 3.10; N, 4.78. Found: C, 36.45; H, 3.10; N, 4.60.

Pt(COD)(met) (6). A 250-mL three-neck round-bottom flask was fitted with a dropping addition funnel in the central neck. The round-bottom flask contained a solution of 0.255 g (0.68 mmol) of Pt(COD)Cl₂ in 40 mL of acetone, and the dropping addition funnel contained 0.054 g (1.40 mmol) of LiOMe dissolved in 10 mL of methanol. A solution of 0.159 g (0.68 mmol) of 4,5-dicarbomethoxy-1,3-dithiol-2-one in 5 mL of THF/methanol (1:1 v/v) was added to the LiOMe solution. This solution was then added dropwise to the Pt(COD)Cl₂ solution, and the reaction was allowed to proceed for 6 h. The solvent volume was reduced to 10 mL, and 20 mL of ether was added. The yellow precipitate, collected by centrifugation, was dissolved in a minimum amount of methylene chloride, and the solution was chromatographed on an alumina column using methylene chloride as eluent. The first yellow band was collected and the solvent volume reduced to 5 mL. Addition of 10 mL of ether resulted in the formation of a yellow precipitate, which was collected and stored under vacuum. IR (KBr, cm⁻¹): 2946 (w, C—H), 1719 and 1701 (s, C=O), 1536 (s) 1427 (s, C=C), 1242 (s). ¹H NMR (CDCl₃): δ 5.525 (s with Pt satellites, 4 H, ²J_{Pt-H} = 26 Hz), 3.804 (s, 6 H), 2.552 (m, 8 H). Anal. Calcd for PtC₁₄H₁₈O₄S₂: C, 33.00; H, 3.56. Found: C, 33.28; H, 3.59.

Pt(P(OMe)₃)₂(met) (7). A solution of 0.063 g (0.50 mmol) of trimethyl phosphite in acetone was added to a solution of 0.1026 g (0.20 mmol) of Pt(COD)(met) in 50 mL of acetone. The solution turned pale yellow immediately. After 6 h, the solvent volume was reduced to 10 mL and an off-white precipitate formed, which was collected by centrifugation, dried with ether, and stored under vacuum. IR (KBr, cm⁻¹): 2999, 2950, and 2848 (w, C—H), 1726 and 1691 (s, C=O), 1535 (s), 1435 (s, C=C), 1242 (s). ¹H NMR (CDCl₃): δ 3.796 (s, 6 H), 3.757 (m, 18 H). ³¹P NMR (CDCl₃): δ 102.98 (¹J_{Pt-P} = 2232 Hz). Anal. Calcd for PtC₁₂H₂₄O₁₀P₂S₂: C, 22.19; H, 3.72; P, 9.54. Found: C, 22.29; H, 3.73; P, 9.65.

Spectroscopic Characterization. ¹H (400 MHz), ¹³C (100.62 MHz), and ³¹P (161.97 MHz) NMR spectra were recorded on a Bruker AMX-400 spectrometer. Chemical shifts are reported downfield from internal solvent peaks: acetone-*d*₆ (δ_H = 2.04) and chloroform-*d*₁ (δ_H = 7.24) for ¹H and chloroform-*d*₁ (δ_C = 77.0) for ¹³C. H₃PO₄ (δ_P = 0) was used as an external standard for ³¹P. Infrared spectra were obtained from KBr pellets on a Mattson Sirius 100 FTIR spectrophotometer. Absorption spectra were recorded on a Hitachi U-2000 UV-visible spectrophotometer. Room-temperature and low-temperature emission measurements were performed on a Spex Fluorolog fluorescence spectrophotometer using a 1-cm × 1-cm quartz fluorescence cell and a liquid nitrogen dewar equipped with quartz windows. Room-temperature lifetimes were measured by single-photon counting, and low-temperature lifetimes were measured by transient digitization; the instrumental setups have been described elsewhere.¹⁷⁻²¹ Low-temperature emission spectra were recorded in DMM (DMF/CH₂Cl₂/MeOH in 1:1:1 v/v/v) and PRP (1-propanol/pentane 2:1 v/v) glasses or in a KBr matrix.

Structure Determinations. Single-crystal X-ray structure determina-

Table 1. Crystallographic Data for Platinum Methylmaleate Dithiolate (met) Complexes

	Pt(Me ₂ bpy)(met)·CHCl ₃ (5)	Pt(P(OMe) ₃) ₂ (met) (7)
chemical formula	C ₁₉ H ₁₉ Cl ₃ N ₂ O ₄ PtS ₂	C ₁₂ H ₂₄ O ₁₀ P ₂ PtS ₂
fw	705.95	649.47
lattice type	monoclinic	monoclinic
space group	P2 ₁ /n (No. 14)	P2 ₁ /c (No. 14)
Z	4	4
a, Å	11.402(1)	11.209(3)
b, Å	9.085(8)	12.250(7)
c, Å	23.041(2)	16.558(4)
α, deg	90	90
β, deg	97.83(5)	102.97(3)
γ, deg	90	90
V, Å ³	2364.7	2215.80
ρ _{calc} , g/cm ³	1.983	1.947
T, °C	-20	25
μ, cm ⁻¹	65.4	67.62
λ _{Mo Kα} (graphite monochromated radiation), Å	0.710 69	0.710 69
R ^a	0.024	0.048
R _w ^a	0.030	0.062

^a R = [Σ||F_o - |F_c||] / [Σ|F_o|]; R_w = [Σw(|F_o - |F_c||)²]^{1/2} / [ΣwF_o²], where w = [σ²(F_o) + (ρF_o²)²]^{-1/2} for the non-Poisson contribution weighting scheme. The quantity minimized was Σw(|F_o - |F_c||)². Source of scattering factors f_o, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

tions were carried out using an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation (λ = 0.710 73 Å) for data collection. Texsan software was used for data reduction, structure solution, and least-squares refinement on a MicroVax II computer.

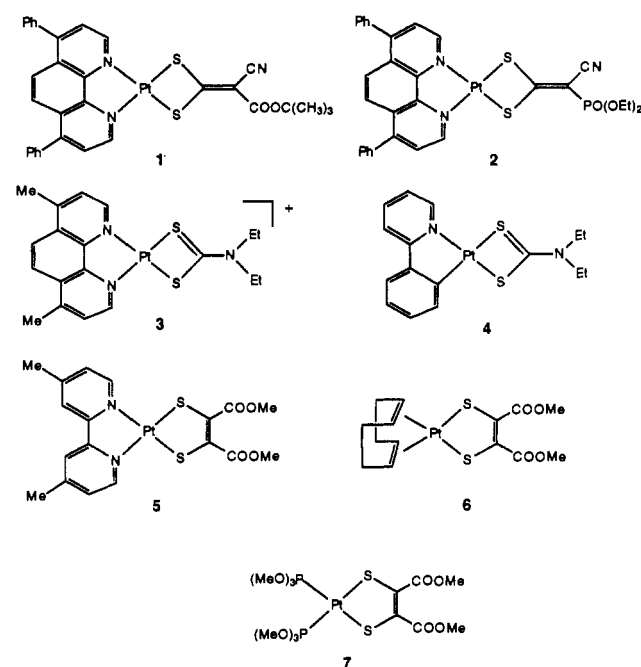
(a) **Pt(Me₂bpy)(met) (5).** A purple hexagonal crystal of Pt(Me₂bpy)(met) (2) (dimensions 0.15 × 0.38 × 0.11 mm³) was grown from a room-temperature chloroform solution. The crystals were found to be air stable at room temperature. Crystal, data collection, and refinement parameters are summarized in Table 1. Heavy-atom methods were used to locate the platinum and two sulfur atoms, while subsequent cycles of least-squares refinements and difference Fourier maps were used to locate the remaining non-hydrogen atoms. Hydrogen atoms were placed at calculated positions.

(b) **Pt(P(OMe)₃)₂(met) (7).** A crystal suitable for X-ray diffraction analysis was grown by slow evaporation of a solution of the complex in chloroform. The crystals were found to be air stable at room temperature. A pale yellow prism (dimensions 0.19 × 0.26 × 0.11 mm³) was mounted on a glass fiber. Crystal, data collection, and refinement parameters are summarized in Table 1. Heavy-atom methods were employed to locate the platinum and two sulfur atoms. The remaining atoms were located using cycles of Fourier maps and least-squares refinements. In the last refinement all non-hydrogen atoms were described with anisotropic thermal parameters. Hydrogen atoms were placed at calculated positions.

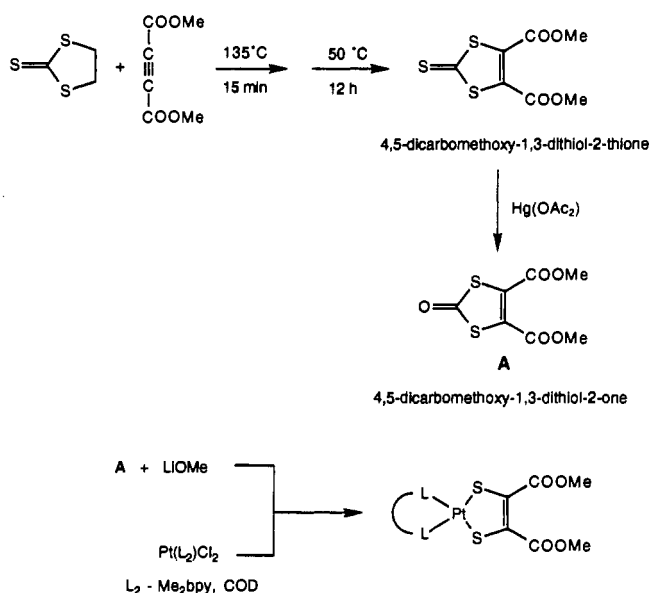
Results and Discussion

The seven complexes studied are shown in Chart 1. Pt(Ph₂phen)(tbcda) (1) was synthesized by following a previously published procedure.¹⁹ Complexes 2, 4, 5, and 6 were readily synthesized by the addition of the dithiolate or dithiocarbamate to the precursor complex Pt(L₂)Cl₂. Complexes 5 and 6 were prepared by the reaction between Pt(L₂)Cl₂ and the met ligand generated *in situ* as described in Scheme 1 based on the earlier work of Brown *et al.*²⁷ Pt(Me₂bpy)(Et₂dtc)⁺ (3) was synthesized by the addition of dithiocarbamate to an aqueous solution of Pt(Me₂bpy)(NO₃)₂ followed by the addition of NaPF₆, while Pt(P(OMe)₃)₂(met) (7) was synthesized by the addition of 2 equiv of trimethyl phosphite to Pt(COD)(met) (6). The resulting complexes are air-stable for months in the solid state, although decomposition in solution occurs over a period of several days when they are exposed to air. The complexes are soluble in most organic solvents but insoluble in ether, hexane, and water. In addition, complexes 3 and 4 are soluble in methanol. The

Chart 1



Scheme 1



complexes were characterized by infrared and ^1H , ^{13}C , and ^{31}P NMR spectroscopies and, in two cases, by X-ray crystallography.

Spectroscopic Characterization. The complexes have distinct IR bands characteristic of the dithiolate or dithiocarbamate ligand. Complexes **1** and **2**, which contain 1,1-dithiolates, have strong IR stretches at ~ 2193 , 1446 , and 1234 cm^{-1} corresponding to ν_{CN} , $\nu_{\text{C}=\text{C}}$, and $\nu_{\text{C}=\text{S}}$ of the dithiolate, respectively. For the met complexes, two strong $\nu_{\text{C}=\text{O}}$ stretches are found between 1719 and 1726 cm^{-1} and between 1691 and 1701 cm^{-1} as well as the $\text{C}=\text{C}$ double-bond stretch at $\sim 1430\text{ cm}^{-1}$.

The ^1H NMR spectra of all of the complexes indicate a square-planar arrangement of ligands around the platinum center. $\text{Pt}(\text{Ph}_2\text{phen})(\text{tbcda})$ (**1**) and $\text{Pt}(\text{Ph}_2\text{phen})(\text{cpdt})$ (**2**) have ^1H NMR spectra that are consistent with the unsymmetrical nature of the dithiolate, in that protons equivalent in the free diimine appear as inequivalent and overlapping resonances. The ^1H resonances corresponding to the dithiolate protons are well resolved and integrate well to the aromatic region. The ^{31}P NMR spectrum of **2** contains a single chemical shift at 12.59 ppm corresponding to the phosphinyl resonance. The structure of $\text{Pt}(2\text{-ppy})(\text{Et}_2\text{-}$

$\text{dtc})$ (**4**) was confirmed by ^1H and ^{13}C NMR spectroscopies. Both NMR spectra are highly resolved with appropriate resonances showing characteristic platinum satellites (^{195}Pt , $I = 1/2$, 33.8% natural abundance). The ^1H NMR spectrum of **4** shows eight distinct proton resonances in the aromatic region ($8.6\text{--}7.0\text{ ppm}$). The most downfield resonance is a doublet with Pt satellites ($\delta 8.597$, 1 H , $^2J_{\text{H-H}} = 6\text{ Hz}$, $J_{\text{Pt-H}} = 19\text{ Hz}$). Four of the next five resonances at 8.082 , 8.010 , 7.680 , and 7.147 ppm are doublets with $^2J_{\text{H-H}} = 8\text{ Hz}$. These resonances show additional proton-proton coupling of 2 Hz and integrate to one proton each. The fifth resonance is a multiplet between 7.31 and 7.27 ppm and, also, integrates to one proton. The remaining resonances are observed as multiplets between 7.1 and 7.0 ppm , integrating to two protons. In addition to these resonances, complex **4** shows two sets of inequivalent methylene (3.825 and 3.784 ppm as quartets with $^3J_{\text{H-H}} = 7\text{ Hz}$) and methyl resonances (1.359 and 1.331 ppm as triplets with $^3J_{\text{H-H}} = 7\text{ Hz}$) for the diethyldithiocarbamate ligand, thus supporting the notion of a planar coordination geometry with Et_2dtc and the unsymmetrical 2-phenylpyridine ligand. In this complex, no hydride resonance is observed down to -20 ppm .

Further support for the coordination of the 2-phenylpyridine ligand through the nitrogen and 2'-carbon atom (Chart 1) is indicated by the ^{13}C NMR spectrum. The ^{13}C attached proton test (APT) NMR spectrum of complex **4** is presented in Figure 1. The spectrum clearly shows 12 distinct carbon resonances in the region between 208 and 118 ppm due to the phenylpyridine ligand and the carbamate carbon of the Et_2dtc ligand. Eight of the resonances are inverted, indicating that they belong to aromatic carbon atoms having a single attached proton, while the other four resonances, located at 208.56 , 166.47 , 146.18 , and 144.79 ppm , remain upright corresponding to carbon atoms having no attached protons in accord with the structure of **4** (Chart 1). From the magnitude of the ^{195}Pt satellites, it is possible to assign the resonances of the carbon atoms having zero attached protons. The resonance of the *ipso* carbon of the phenyl ring directly attached to the Pt atom has the largest satellites and occurs at 146.18 ppm . The resonances at 166.47 and 144.79 ppm correspond to the carbons α to the N of the pyridine and α to the *ipso* carbon of the phenyl, respectively. The resonance at 208.56 ppm is assigned to the carbamate carbon of the Et_2dtc ligand on the basis of its downfield position. This assignment is in accord with the corresponding resonance for $\text{Pt}(\text{Et}_2\text{dtc})_2$ that occurs at 211.5 ppm .²⁸ In addition to these resonances are the resonances due to the aliphatic carbons of the Et_2dtc ligand. The methylene carbons exhibit two distinct resonances located at 45.85 and 44.64 ppm , while the two methyl carbons appear as a broad and unresolved resonance located at 12.44 ppm .

The square-planar geometry about platinum was confirmed by single-crystal X-ray diffraction studies for two of the met complexes. ORTEP diagrams of $\text{Pt}(\text{Me}_2\text{bpy})(\text{met})\text{-CHCl}_3$ (**5**) and $\text{Pt}(\text{P}(\text{OMe})_3)_2(\text{met})$ (**7**) are shown as Figures 2 and 3, respectively. Final refined positional and thermal parameters for **5** and **7** are given in Tables 2 and 3, respectively, and selected bond distances and angles for both structures are presented in Table 4. The supplementary material contains the final anisotropic thermal parameters, calculated hydrogen positional parameters, and a complete tabulation of bond distances and angles.

The basic structure of $\text{Pt}(\text{Me}_2\text{bpy})(\text{met})$ (**5**) is that of a slightly distorted square plane around the Pt center. The bpy chelate results in a N-Pt-N bond angle of $79.8(2)^\circ$, which is significantly less than the idealized value of 90° . The average Pt-N distance of $2.055(1)\text{ \AA}$ is within the range of those for other platinum diimine complexes. Typical Pt-N bond lengths for complexes of the type $\text{Pt}(\text{N-N})\text{X}_2$ where N-N is 2,2'-bipyridine or 2,2'-bipyrimidine and X is mesityl or CN are in the range $2.04(6)\text{--}$

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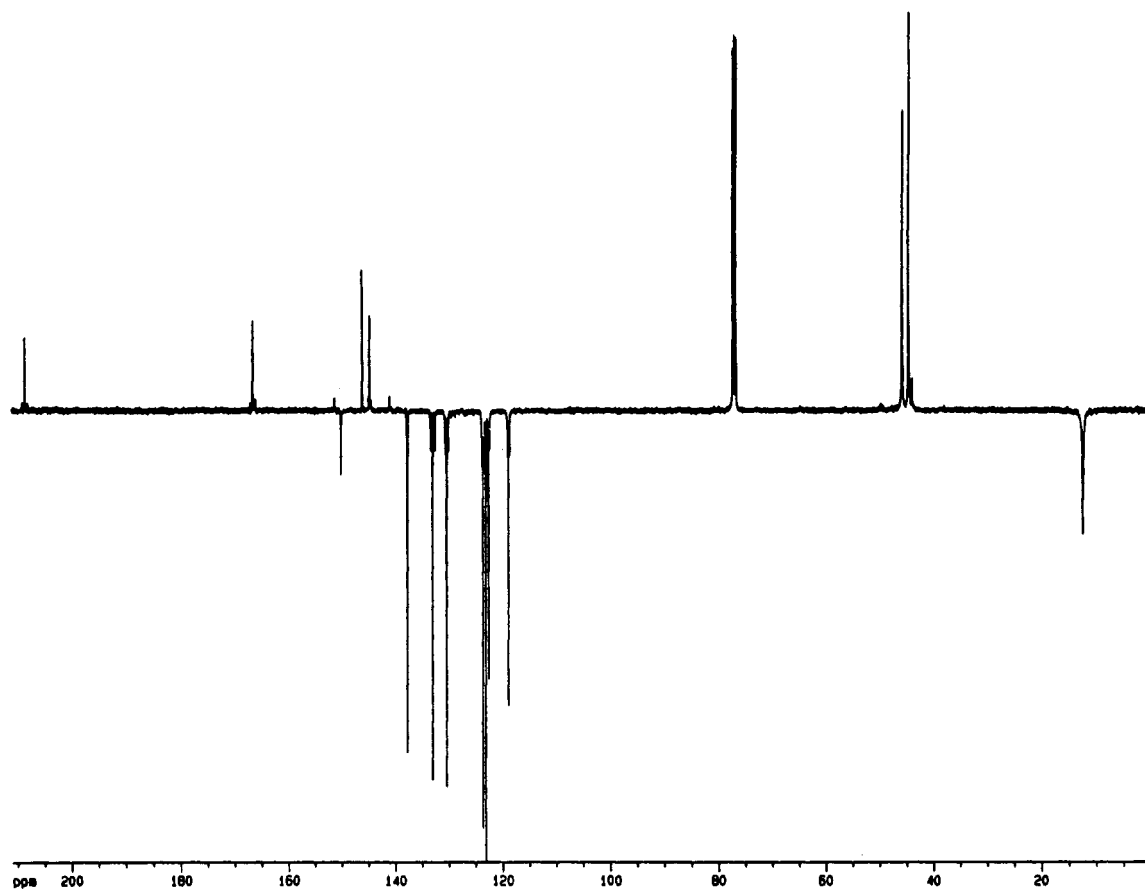


Figure 1. ^{13}C NMR spectrum of $\text{Pt}(2\text{-phy})(\text{Et}_2\text{dtc})$ (**4**) indicating the unsymmetrical nature of the 2-phenylpyridine ligand. The spectrum was collected using the attached proton test (APT) pulse sequence. Carbon resonances phased positive have zero or two attached protons, while those with negative phasing have one or three attached protons.

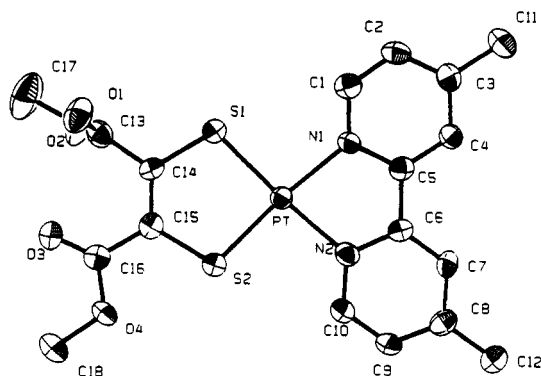


Figure 2. Molecular structure and atom numbering of the non-hydrogen atoms (ORTEP diagram, 50% thermal ellipsoids) of $\text{Pt}(\text{Me}_2\text{bpy})(\text{met})$ (**5**).

2.09(1) Å.^{29,30} The longer Pt–S distances (2.245(2) and 2.244(2) Å) allow the S–Pt–S bond angle to be 89.29(7).

In comparison, the structure of $\text{Pt}(\text{P}(\text{OMe})_3)_2(\text{met})$ (**7**) is less distorted than **5** in the square plane around the Pt center. The P–Pt–P, P–Pt–S, and S–Pt–S bond angles are all close to 90°, being 95.2(1), 89.7(1), 86.8(1), and 88.4(1)°, respectively. The Pt–P bond lengths of 2.239(4) and 2.238(2) Å and Pt–S bond lengths of 2.302(4) and 2.300(4) Å for **7** are comparable to bond distances in similar complexes that have *trans* phosphorus and sulfur ligands. For example, typical Pt–P and Pt–S bond distances for complexes of the type $\text{PtLL}'(\text{S-S})$ (L, L' = PPh_3 , Cl, C(O)-

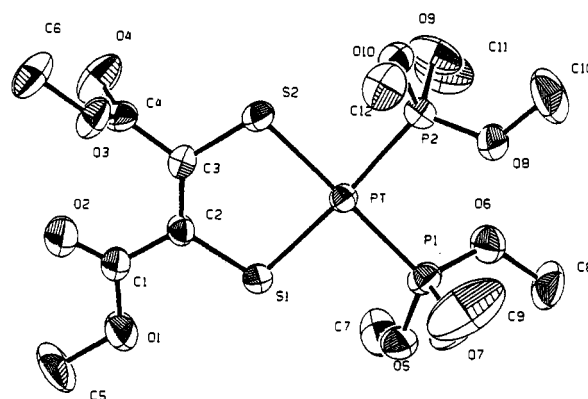


Figure 3. Molecular structure and atom numbering of the non-hydrogen atoms (ORTEP diagram, 50% thermal ellipsoids) of $\text{Pt}(\text{P}(\text{OMe})_3)_2(\text{met})$ (**7**).

Me, dppe; S–S = CS_2 , dithiocarbamate, dithiolate) are in the ranges 2.24–2.28 and 2.29–2.35 Å, respectively.^{31–34,36}

The met chelate bond distances and angles are similar within complexes **5** and **7** and are close to those in the related $\text{Ni}(\text{met})_2^{2-}$ complex.²⁷ In addition, the bond distances are in the range of those for analogous metal bis(mnt) complexes (mnt = maleoni-

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Table 2. Positional Parameters and B_{eq} Values for Pt(Me₂bpy)(met) (5)^a

atom	x	y	z	$B_{eq}, \text{\AA}^2$ ^b
Pt	0.10773(3)	0.40494(3)	0.44615(1)	2.30(1)
S1	-0.0451(2)	0.3851(2)	0.37407(8)	2.94(9)
S2	0.1998(2)	0.5518(2)	0.38837(8)	2.87(9)
O1	-0.1008(5)	0.4125(6)	0.2260(2)	4.6(3)
O2	-0.1657(5)	0.6176(7)	0.2643(2)	4.8(3)
O3	0.0670(5)	0.6805(6)	0.2297(2)	4.2(3)
O4	0.2411(5)	0.7088(6)	0.2864(2)	3.9(3)
N1	0.0390(5)	0.2692(6)	0.5046(2)	2.4(3)
N2	0.2371(5)	0.4224(6)	0.5170(3)	2.7(3)
C1	-0.0623(7)	0.1946(8)	0.4967(3)	3.0(4)
C2	-0.1029(6)	0.1103(8)	0.5390(3)	3.1(4)
C3	-0.0372(7)	0.1002(8)	0.5937(3)	3.0(4)
C4	0.0701(7)	0.1743(8)	0.6025(3)	2.9(4)
C5	0.1068(6)	0.2586(8)	0.5581(3)	2.6(3)
C6	0.2173(6)	0.3424(8)	0.5650(3)	2.4(3)
C7	0.2969(7)	0.3492(8)	0.6158(3)	2.8(3)
C8	0.3960(7)	0.4384(8)	0.6203(3)	3.2(4)
C9	0.4092(7)	0.519(1)	0.5713(4)	3.9(4)
C10	0.3332(7)	0.508(1)	0.5212(3)	3.6(4)
C11	-0.0792(8)	0.013(1)	0.6428(4)	4.0(4)
C12	0.4798(7)	0.452(1)	0.6762(4)	4.0(4)
C13	-0.0946(7)	0.502(1)	0.2645(4)	3.2(4)
C14	-0.0070(6)	0.4966(8)	0.3187(3)	2.3(3)
C15	0.0974(7)	0.5687(8)	0.3246(3)	2.6(3)
C16	0.1306(7)	0.6583(8)	0.2751(3)	2.7(4)
C17	-0.2462(9)	0.638(1)	0.2115(4)	6.8(6)
C18	0.2822(8)	0.798(1)	0.2411(4)	4.8(5)
C11	-0.1123(2)	0.5543(4)	0.0645(1)	7.0(2)
C12	0.1275(2)	0.6691(3)	0.0785(1)	5.8(1)
C13	0.0872(2)	0.3626(3)	0.0990(1)	6.0(1)
C19	0.0309(8)	0.540(1)	0.1036(4)	4.4(4)

^a The figures in parentheses correspond to the estimated standard deviations in the least significant digits. ^b The equivalent isotropic temperature factors B_{eq} are defined as

$$B_{eq} = \frac{8\pi^2}{3} \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* \hat{a}_i \hat{a}_j$$

where U_{ij} are the anisotropic thermal parameters and a_i^* and a_j are the reciprocal and real lattice constants, respectively. The parameters U_{ij} are defined as

$$\exp(-2\pi^2(a^*2U_{11}h^2 + b^*2U_{22}k^2 + c^*2U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

trilethiolate), indicating that the met ligand displays delocalization throughout the chelate ring. The S-C bond lengths (1.731(8) and 1.755(7) Å for **5** and 1.75(1) and 1.73(1) Å for **7**) are in the range of those found in metal-mnt complexes (1.70–1.79 Å) where M = Ni(II), Pt(II), Co(II), and Cu(I), indicating that similar delocalizations exist in metal-met and metal-mnt complexes and that the shorter S-C bond length relative to the single-bond value (1.78 Å) for an sp², hybridized C is independent of coordinated metal and metal oxidation state. The C14-C15 and C2-C3 bond lengths (1.35(1) and 1.34(1) Å for **5** and **7**, respectively) are typical of a C=C double bond in each Pt(met) chelate ring. Interestingly, the two carbomethoxy groups in each structure are orthogonal, with one group essentially lying in the plane defined by Pt, S1, and S2 and the other group perpendicular to this plane.

Solvent Dependence of the Absorption Spectroscopy. The energy of the lowest electronic absorption band shows marked

Table 3. Positional Parameters and B_{eq} Values for Pt(P(OMe)₃)₂(met) (7)^a

atom	x	y	z	$B_{eq}, \text{\AA}^2$
Pt	0.23458(3)	0.01478(3)	-0.14935(2)	2.46(2)
S1	0.2679(3)	-0.1309(2)	-0.2293(2)	3.3(1)
S2	0.2572(3)	-0.1024(2)	-0.0384(2)	3.4(1)
P1	0.2047(3)	0.1225(2)	-0.2613(2)	3.4(1)
P2	0.2067(2)	0.1471(2)	-0.0622(2)	3.0(1)
O1	0.309(1)	-0.3518(7)	-0.2694(5)	5.6(4)
O2	0.313(1)	-0.4308(8)	-0.1506(5)	7.6(6)
O3	0.4015(7)	-0.3366(6)	0.0213(5)	4.5(4)
O4	0.1982(8)	-0.3656(8)	-0.0050(6)	5.8(4)
O5	0.1740(7)	0.0639(7)	-0.3483(4)	4.4(4)
O6	0.0981(7)	0.2057(6)	-0.2620(5)	4.3(3)
O7	0.3151(9)	0.1895(9)	-0.2779(6)	6.9(5)
O8	0.2348(7)	0.2636(6)	-0.0913(5)	4.1(3)
O9	0.0785(7)	0.1529(8)	-0.0396(5)	5.5(4)
O10	0.2834(7)	0.1357(6)	0.0309(4)	3.7(3)
C1	0.304(1)	-0.3497(8)	-0.1905(7)	3.7(5)
C2	0.2838(9)	-0.2416(8)	-0.1607(6)	2.7(4)
C3	0.2786(9)	-0.2281(8)	-0.0812(6)	2.8(4)
C4	0.287(1)	-0.319(1)	-0.0197(6)	3.7(5)
C5	0.330(2)	-0.459(1)	-0.3014(9)	9(1)
C6	0.420(1)	-0.423(1)	0.0829(8)	5.8(7)
C7	0.062(1)	0.007(1)	-0.3748(8)	5.4(6)
C8	0.061(1)	0.286(1)	-0.3282(9)	5.8(7)
C9	0.408(2)	0.229(2)	-0.228(1)	12(1)
C10	0.223(2)	0.360(1)	-0.043(1)	8(1)
C11	-0.031(1)	0.139(1)	-0.100(1)	7.0(8)
C12	0.416(1)	0.142(1)	0.0466(8)	5.4(6)

^a See footnotes a and b of Table 2.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Pt(Me₂bpy)(met) (5) and Pt(P(OMe)₃)₂(met) (7)^a

Pt(Me ₂ bpy)(met) (5)		Pt(P(OMe) ₃) ₂ (met) (7)	
Distances			
Pt-S1	2.245(2)	Pt-S1	2.302(4)
Pt-S2	2.244(2)	Pt-S2	2.300(4)
Pt-N1	2.058(6)	Pt-P1	2.239(4)
Pt-N2	2.051(6)	Pt-P2	2.238(4)
N1-C5	1.33(1)	P1-O5	1.577(8)
N2-C6	1.368(9)	P2-O8	1.561(8)
C5-C6	1.46(1)	O5-C7	1.42(2)
		O8-C10	1.45(2)
S1-C14	1.731(8)	S1-C2	1.75(1)
S2-C15	1.755(7)	S2-C3	1.73(1)
C14-C15	1.35(1)	C2-C3	1.34(1)
C13-C14	1.49(1)	C1-C2	1.45(1)
C15-C16	1.49(1)	C3-C4	1.49(1)
C13-O1	1.20(1)	C1-O2	1.18(1)
C13-O2	1.32(1)	C1-O1	1.32(1)
O2-C17	1.43(1)	O1-C5	1.45(2)
C16-O3	1.21(1)	C4-O4	1.22(2)
C16-O4	1.33(1)	C4-O3	1.33(1)
O4-C18	1.45(1)	O3-C6	1.45(2)
Angles			
N1-Pt-N2	79.8(2)	P1-Pt-P2	95.2(1)
S1-Pt-S2	89.29(7)	S1-Pt-S2	88.4(1)
Pt-N1-C5	114.4(5)		
Pt-N2-C6	115.0(5)		
Pt-S1-C14	104.5(2)	Pt-S1-C2	103.5(4)
Pt-S2-C15	103.7(3)	Pt-S2-C3	103.2(4)
N1-Pt-S1	96.3(2)	S1-Pt-P1	89.7(1)
N2-Pt-S2	94.7(2)	S2-Pt-P2	86.8(1)

^a Atom labels are given according to Figures 2 and 3 for **5** and **7**, respectively. Estimated standard deviations are given in parentheses.

differences between one set of complexes that contains an α, α' -diimine ligand (**1**, **2**, **3**, and **5**) and the other set of complexes that does not (**4**, **6**, and **7**). The former are highly colored as solids and in solution show several intense absorptions at higher energies ($\lambda > 350$ nm, 33.3×10^3 cm⁻¹) as well as a strong absorption band in the 450–650-nm ($(22.2\text{--}15.4) \times 10^3$ cm⁻¹) region of the spectrum ($\epsilon > 10$ 000 M⁻¹ cm⁻¹). The energy of the lowest energy absorption band in solution increases directly with solvent polarity,

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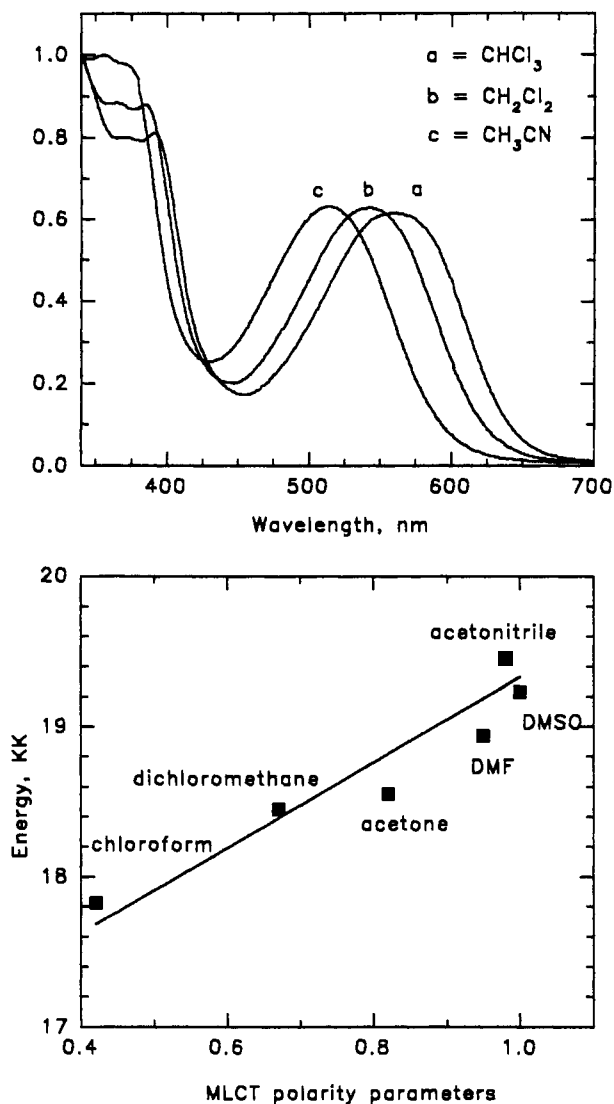


Figure 4. (a) Absorption spectra of Pt(Me₂bpy)(met) (5) in solvents of differing polarity and (b) the correlation of the lowest energy absorption band with the solvent polarity parameters put forth by Lees.⁴¹

Table 5. Electronic Absorption Maxima as a Function of Solvent for the Platinum Complexes

complex	no.	λ_{abs} , nm (10^3 cm^{-1})	
		CHCl ₃	CH ₃ CN
Pt(Ph ₂ phen)(tbcda)	1	471 (21.2)	439 (22.8)
Pt(Ph ₂ phen)(cpdt)	2	468 (21.4)	435 (23.0)
Pt(Me ₂ bpy)(Et ₂ dtc) ⁺	3	380 (26.3)	369 (27.1)
Pt(2-bhpy)(Et ₂ dtc)	4	378 (26.4)	374 (26.7)
Pt(Me ₂ bpy)(met)	5	571 (17.5)	515 (19.4)
Pt(COD)(met)	6	399 (25.1)	395 (25.3)
Pt(P(OMe) ₃) ₂ (met)	7	326 (30.7)	324 (30.9)

as shown for Pt(Me₂bpy)(met) (5) in Figure 4. An excellent correlation of absorption band energy with solvent polarity is found using Lees' E^*_{MLCT} scale,⁴³ based on a reference charge-transfer transition. The lowest energy absorption maxima for these complexes are listed in Table 5. As shown by Figure 4, the absorption maximum of 5 shifts quite substantially from 571 nm ($17.5 \times 10^3 \text{ cm}^{-1}$) in chloroform to 515 nm ($19.4 \times 10^3 \text{ cm}^{-1}$) in acetonitrile. Even though Pt(Me₂bpy)(Et₂dtc)⁺ (3) is cationic, its lowest energy absorption maximum shifts from 380 nm ($26.3 \times 10^3 \text{ cm}^{-1}$) in CHCl₃ to 369 nm ($27.1 \times 10^3 \text{ cm}^{-1}$) in MeCN. In general, solvatochromism is indicative of a large change in the polarity of the molecule between the ground and excited states

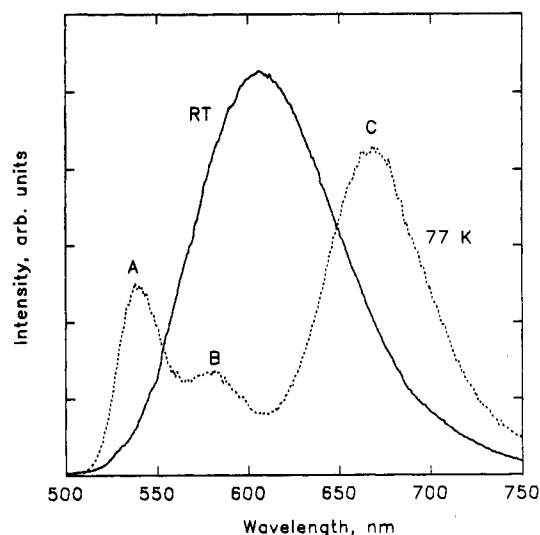


Figure 5. Emission spectrum in DMM at (—) room temperature and (---) 77 K of Pt(Ph₂phen)(tbcda) (1).

and is often observed for charge transfer transitions.^{44–46} This suggests that complexes 1, 2, 3, and 5 undergo a charge-transfer transition similar to that reported previously for the Pt(diimine)-(mnt) and Pt(diimine)(ecda) complexes.^{18–20} In contrast, the lowest energy absorption maxima of complexes 4, 6, and 7 change only slightly with increasing solvent polarity. For example, the lowest energy absorption band of Pt(COD)(met) (6) changes from 345 nm ($29.0 \times 10^3 \text{ cm}^{-1}$) in CHCl₃ to 339 nm ($29.5 \times 10^3 \text{ cm}^{-1}$) in MeCN.

In all of the complexes studied, the higher energy transitions ($\lambda_{\text{abs}} < 350 \text{ nm}$, $28.6 \times 10^3 \text{ cm}^{-1}$) are similar to those in either the free ligands or the parent Pt(L₂)Cl₂ complexes that have been assigned as either intraligand diimine, intraligand dithiolate, or Pt(diimine) MLCT and are not considered further in this report.

Temperature and Solvent Dependence of the Emission Spectroscopy. All of the complexes that contain a diimine ligand are luminescent in solution at room temperature, while Pt(COD)(met) (6) and Pt(P(OMe)₃)₂(met) (7) emit only at low temperature. Emission spectra for the complexes depend on the S-donor ligand. The complexes that contain a diimine and either a 1,1-dithiolate or a dithiocarbamate ligand, Pt(Ph₂phen)(tbcda) (1), Pt(Ph₂phen)(cpdt) (2), and Pt(Me₂bpy)(Et₂dtc)⁺ (3), exhibit a broad emission band in fluid solution with λ_{max} between 590 and 610 nm ($(16.9\text{--}16.4) \times 10^3 \text{ cm}^{-1}$) and no discernible vibronic structure. The emission energy of these complexes is independent of solvent polarity, in contrast with their respective absorption spectra. For example, the lowest energy absorption band of Pt(Ph₂phen)(tbcda) (1) blue-shifts $\sim 60 \text{ nm}$ from chloroform to acetonitrile solvent, while a change of only $\sim 5 \text{ nm}$ is observed in the corresponding emission spectrum. Pt(2-phpy)(Et₂dtc) (4) shows emissive properties different from those of the other complexes and will be discussed separately.

The emission spectra of complexes 1–3 in DMM glass (DMF/CH₂Cl₂/MeOH 1:1:1 v/v/v), change on going from room temperature to 77 K. For Pt(Ph₂phen)(tbcda) (1) and Pt(Ph₂phen)(cpdt) (2), a large shift to lower energy of $\sim 1481 \text{ cm}^{-1}$ occurs upon glassing of the medium and below 100 K two higher energy bands (labeled A and B in Figure 5 for 1) appear. Bands A and B for 1 are broad and centered at 537 nm ($18.6 \times 10^3 \text{ cm}^{-1}$) and 577 nm ($17.3 \times 10^3 \text{ cm}^{-1}$), with a separation of $\sim 1300 \text{ cm}^{-1}$ (Figure 5). For Pt(Me₂bpy)(Et₂dtc)⁺ (3), a shift to higher energy of $\sim 300 \text{ cm}^{-1}$ occurs upon glassing and two higher energy bands (labeled A and B in Figure 6) appear. Bands A and B at 474 nm ($21.1 \times 10^3 \text{ cm}^{-1}$) and 506 nm ($19.8 \times 10^3 \text{ cm}^{-1}$), respectively,

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Table 6. Emission Maxima at Room Temperature and 77 K in DMM Glass

complex	RT λ_{em} , nm (10^3 cm^{-1})	77 K λ_{em} , nm (10^3 cm^{-1})		
		A	G	C
Pt(Ph ₂ phen)(tbcda) (1)	605 (16.5)	537 (18.6)	578 (17.3)	668 (15.0)
Pt(Ph ₂ phen)(cpdt) (2)	594 (16.8)	537 (18.6)	575 (17.4)	648 (15.4)
Pt(Me ₂ bpy)(Et ₂ dtc) ⁺ (3)	590 (16.9)	474 (21.2)	506 (19.8)	564 (17.7)
Pt(2-phpy)(Et ₂ dtc) (4)	455 (22.0) 503 (19.9) 532 (18.9)	492 (20.3), 529 (18.9), 563 (17.8) ^a		
Pt(Me ₂ bpy)(met) (5)	663 (15.1) 708 (14.1)	634 (15.8), 695 (14.4) ^a		
Pt(COD)(met) (6)		620 (16.1), 675 (14.8) ^a		
Pt(P(OMe) ₃) ₂ (met) (7)		625 (16.0), 680 (14.7) ^a		

^a Emission maxima of all bands illustrating the vibrational progression in these complexes.

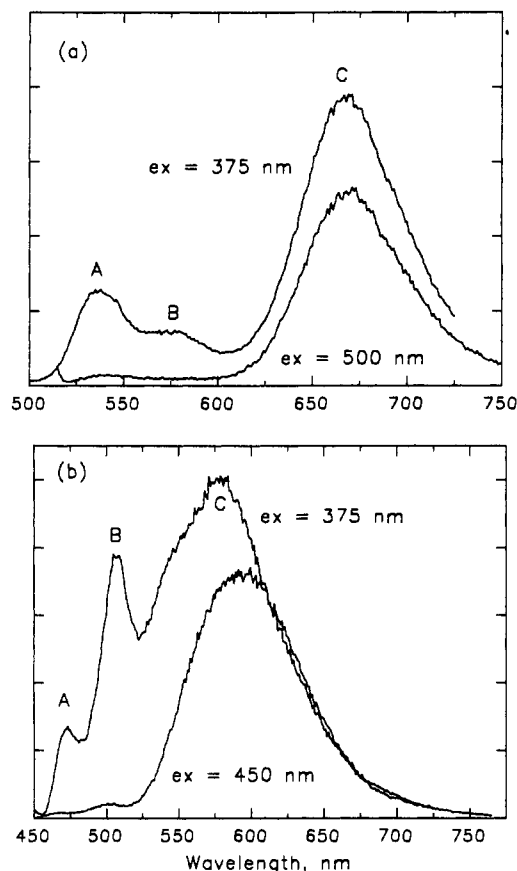


Figure 6. Wavelength dependence of emission spectra at 77 K in DMM glass of (a) Pt(Ph₂phen)(tbcda) (1) and (b) Pt(Me₂bpy)(Et₂dtc)⁺ (3).

are separated by ~ 1300 cm^{-1} . Emission maxima are given in Table 6.

Different excitation spectra for 1–3 are obtained at 77 K, depending on the collection wavelength. Collection at either emission band A or B (Figure 5 or 6) results in a structured excitation spectrum with a distinct low-energy band. In contrast, collecting at band C (Figure 5 or 6) yields a broad and unstructured excitation spectrum.

Similarly, the observed emission spectra are dependent upon excitation wavelength. This is shown in Figure 6 for Pt(Ph₂phen)(tbcda) (1) and Pt(Me₂bpy)(Et₂dtc)⁺ (3). For example, if Pt(Me₂bpy)(Et₂dtc)⁺ (3) is excited at 450 nm rather than 375 nm, only the low-energy band C is observed (Figure 6). The complex Pt(Ph₂phen)(tbcda) (1) has behavior virtually identical to that of 3 with the only difference being the position of the emission bands. The emission spectrum of Pt(Ph₂phen)(cpdt) (2) differs slightly from those of 1 and 3. Specifically, the three emission bands of 2 are less well-resolved and the intensity of band C is lower than that of band A (or B), although the positions

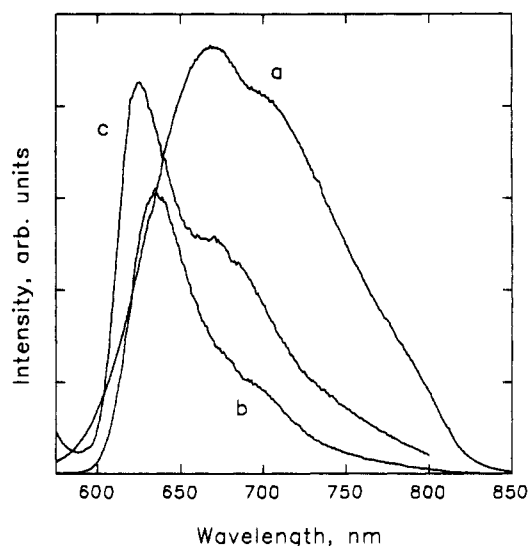


Figure 7. Emission spectra of Pt(Me₂bpy)(met) (5) (a) at room temperature in a DMM solution, (b) at 77 K in DMM glass, and (c) at 77 K in the solid state.

of bands A and B are identical to those for 1 (535 and 576 nm, respectively).

The emission spectra of the met complexes are simpler than those of complexes 1–3 discussed above. All three of the met complexes exhibit strong emission in rigid media and in the solid state at 77 K, but only Pt(Me₂bpy)(met) (5) shows luminescence in fluid solution. Figure 7 illustrates the room-temperature and 77 K emission spectra for Pt(Me₂bpy)(met) (5). Although the 77 K emission spectrum of 5 in DMM is more resolved than the spectrum at room temperature, vibronic structure is not well-resolved. The solid-state emission spectrum of 5 at 77 K exhibits a well-resolved vibrational progression of 1175 cm^{-1} . Similar low-temperature emission spectra are observed for Pt(COD)(met) (6) and Pt(P(OMe)₃)₂(met) (7), although the vibrational progression is less resolved than for 5, even in the solid state. Unlike the wavelength dependence of the emission and excitation spectra of complexes 1–3, the emission and excitation spectra of complexes 5–7 do not change with excitation wavelength.

Assignment of the Emitting State. From the spectroscopic data described above and on the basis of previously reported assignments of excited states in related complexes, it is possible to develop a consistent set of assignments for the lowest energy absorption band and for the emissive excited state of the platinum complexes reported here. First it will be helpful to group the complexes described here into three classes. Class I includes the 1,1-dithiolate and dithiocarbamate complexes containing α,α' -diimines, complexes 1–3. Class II contains all of the 1,2-dithiolate complexes of met, complexes 5–7. Finally the third class consists of the single 2-phenylpyridine complex, Pt(2-phpy)(Et₂dtc) (4). The complexes within each class have very similar spectroscopic

properties and are comparable to complexes already characterized in the literature.

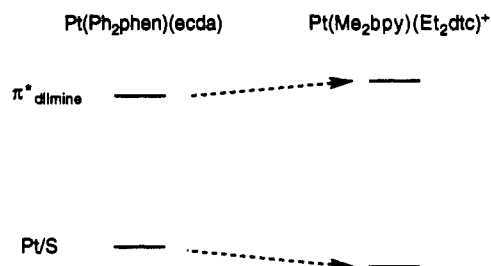
Class I. Class I complexes are solvatochromic, with complexes 1 and 2 exhibiting the largest blue shift in absorption energy as the polarity of the solvent increases. This effect is due to the interaction of a large ground-state dipole with the solvent.⁴⁷ As the solvent polarity increases, the ground state becomes increasingly stabilized, leading to a shift in the absorption maximum to higher energy. Pt(Me₂bpy)(Et₂dtc)⁺ (3) is also solvatochromic but less so than 1 or 2. The shift in λ_{abs} for 3 is only -11 nm (800 cm⁻¹) as the solvent is changed from chloroform to acetonitrile, while for 1 and 2 the shift is -32 nm (1600 cm⁻¹). The smaller shift is likely due to 3 being cationic, so that charge-dipole interactions with the solvent compete with the effect of dipole-dipole interactions and diminish it.

As noted previously for 1-3, the emission spectra change as the temperature is lowered from room temperature to 77 K. Specifically at 77 K, two new bands appear at lower energy (labeled A and B in Figure 5 or 6). To show that these bands are due to complexes 1-3, the complexes were recrystallized from methylene chloride and chromatographed through silica gel. After these purification steps, the spectra did not change. In addition, the 77 K emission spectra of the respective precursor complexes, Pt(L₂)Cl₂, were examined under identical conditions to rule out the possibility of unreacted starting material contamination. Emission from Pt(L₂)Cl₂ occurs 20-50 nm to the red, indicating that the new emission bands are due to the respective platinum dithiolate complex.

The spectroscopic behavior described above is similar in almost all respects to that of the Pt(diimine)(ecda) complexes (ecda is the ethyl ester analog of tbcda) reported previously.¹⁸⁻²⁰ Like 1-3, the Pt(diimine)(ecda) complexes exhibit a highly solvent-dependent absorption in the 400-500 nm ((25.0-20.0) × 10³ cm⁻¹) region of the spectrum, which has been shown through systematic ligand variation to arise from a Pt(d)/S(p)- π^* _{diimine} charge transfer. The intense solvent-dependent absorption band present in the spectra of these complexes is found to be absent in spectra of related complexes containing a saturated diamine in place of the diimine or in Pt(diimine)Cl₂ systems that do not contain a thiolate donor. These observations indicate a requirement of an unsaturated diimine and a sulfur donor for the solvatochromic transition, which in turn suggests the LUMO is mainly of π^* (diimine) character while the HOMO contains a significant sulfur lone pair contribution. This experimental conclusion for the ecda complexes is supported by extended Hückel molecular orbital calculations performed on model Pt(diimine)-(dithiolate) systems.²⁰ Thus, by analogy with the previously studied diimine ecda complexes, the solvatochromic transition in complexes 1-3 is assigned as a (Pt(d)/S(p)- π^* _{diimine}) charge transfer.

A key similarity between complexes 1-3 and the Pt(diimine)(ecda) complexes reported previously is the temperature dependence of emission spectra. For Pt(Ph₂phen)(ecda), for example, a featureless emission band at room temperature with $\lambda_{\text{em}} \sim 600$ nm (16.7 × 10³ cm⁻¹) exhibits a sharp decrease of ~ 1300 cm⁻¹ in emission energy upon glassing of the solvent (165 K) and emergence of two new higher energy emission bands upon subsequent cooling. The two new bands are located at 537 and 580 nm (18.6 × 10³ and 17.2 × 10³ cm⁻¹) and increase in intensity until 80 K, while the intensity of the band at 650 nm (15.4 × 10³ cm⁻¹) remains relatively constant over the same temperature range. Upon further cooling to less than 20 K, the intensity of the two new bands remains relatively constant, while the intensity of the band at 650 nm (15.4 × 10³ cm⁻¹) decreases dramatically. The two new bands, which are separated by ~ 1360 cm⁻¹, have identical lifetimes that differ from that of the band at 650 nm (15.4 × 10³ cm⁻¹). These bands are the same as those seen for complexes 1

Scheme 2



and 2 at 77 K (see bands A and B in Figure 5) and have been assigned as a ³(π - π^*) excited state of the diimine ligand. Support for the notion that the two bands located at 537 and 580 nm belong to the same excited state which differs from the excited state of the 650-nm band lies in the fact that excitation spectra vary depending upon the collection wavelength. When the emission is monitored at either 537 or 580 nm, the same excitation spectrum results, whereas when the emission is collected at 650 nm, a different, less structured excitation spectrum is obtained. The band at 650 nm, which corresponds to band C for complexes 1 and 2 (see Figure 5), has been assigned as the triplet state of the solvent-dependent absorption, ³(Pt(d)/S(p)- π^* _{diimine}).

The completely analogous results for complexes 1 and 2 relative to those for Pt(diimine)(ecda) derivatives allows parallel assignments for the emitting states of 1 and 2 to be made. The energies of the ³(Pt(d)/S(p)- π^* _{diimine}) bands (labeled C in Figure 5) are similar for 1, 2, and Pt(Ph₂phen)(ecda), being 668, 648, and 651 nm at 77 K, respectively. The small difference in energy is related to slight differences in the ligand field strength of the three different 1,1-dithiolates.

The energies of bands A, B, and C for 3 are different from those of 1 and 2 but consistent with values expected for analogous excited states in a complex having Me₂bpy as the diimine rather than Ph₂phen and an overall positive charge. For 3, bands A and B are expected to occur at higher energy because the ³(π - π^* _{diimine}) transition in Me₂bpy is higher in energy than the corresponding transition in Ph₂phen. In addition, band C also occurs at higher energy because of the cationic nature of 3 and the effect of the positive charge on the highest occupied molecular orbital. Scheme 2 illustrates the effects of changing the diimine from Ph₂phen to Me₂bpy and the S-donor ligand from a 1,1-dithiolate to a dithiocarbamate. Changing from a phenanthroline to bipyridine diimine raises the π^* _{diimine} orbital of 3 relative to 1 and 2, while the cationic charge leads to stabilization of the filled frontier orbitals, including the Pt(d)/S(p) HOMO. The overall effect is to raise the energy of band C for 3 relative to 1 and 2.

The absorption and emission behaviors of 1-3 are entirely consistent with the absorption and emission behaviors exhibited by Pt(Ph₂phen)(ecda). On this basis, the assignments of the excited states of bands A, B, and C for 1-3 are as follows: bands A and B correspond to a ³(π - π^* _{diimine}) state, while band C is a ³(Pt(d)/S(p)- π^* _{diimine}) charge transfer.

Class II. Class II complexes all contain the dianionic met ligand and are luminescent in rigid media at 77 K. The 77 K emission spectra of complexes 5-7 show evidence of a vibrational progression that is most pronounced in the solid state. The complex Pt(Me₂bpy)(met) (5) exhibits the additional properties of being solvatochromic and luminescent in fluid solution at room temperature. The nature of the solvatochromic band (Figure 4) that was discussed above applies to this complex as well because it satisfies the necessary conditions of having an unsaturated diimine ligand and a S-donor ligand.

The poorly resolved vibrational progression of 1175 cm⁻¹ for complexes 5-7 is reminiscent of the Pt complexes containing the 1,2-dithiolate mnt that is analogous to met with cyano substituents in place of the carbomethoxy groups. All of the mnt complexes, including the PtL₂(mnt) complexes where L₂ is a diphosphine

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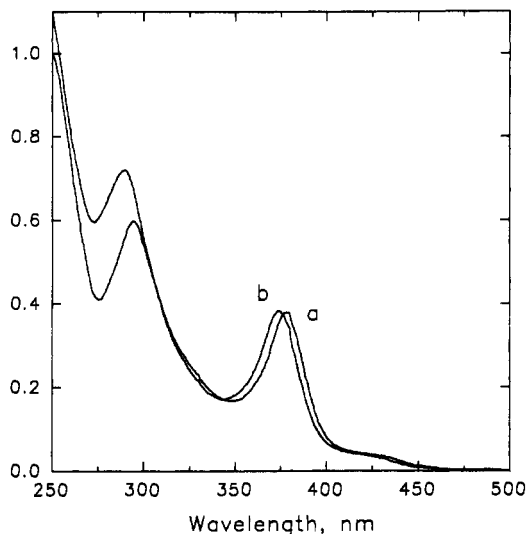


Figure 8. Electronic absorption spectra of Pt(2-ppy)(Et₂dtc) (**4**) in (a) methylene chloride and (b) acetonitrile solution.

chelate, bis(phosphine) ligands, COD, and diimine chelates and the anionic Rh(I) and Ir(I) complexes MLL'(mnt)⁻ where L and L' are neutral 2e⁻ donors exhibit vibrational structure in both their emission and excitation spectra. The presence of this structure in the emission of all mnt complexes is thus independent of both metal and non-mnt ligands. The similarity of the emission and excitation spectra for all of the mnt complexes indicates that they possess a common emitting state of ³(Pt(d)/S(p)-π*_{dithiolate}) character. Although, the vibrational structure exhibited by the met complexes is not as well resolved as that for the mnt complexes, possibly due to the greater flexibility and additional oscillators within the met ligand including ν_{C=O}, it is evident that the same emissive excited state occurs in the met complexes, so that this state is assigned as ³(Pt(d)/S(p)-π*_{met}).

Class III. The electronic absorption spectra of Pt(2-ppy)(Et₂dtc) (**4**) is shown in Figure 8. The 2-phenylpyridine ligand shows ultraviolet absorption transitions (λ < 300 nm) that are characteristic of π-π* ligand-localized transitions.^{10,48} Absorption transitions at wavelengths greater than 350 nm for transition metal complexes containing α-C-deprotonated 2-ppy are not ligand-localized transitions but MLCT transitions on the basis of the energy and intensity of these absorption bands. Support for these assignments comes from related complexes whose spectra contain similar absorption bands. The absorption spectrum of **4**, shown in Figure 8, is similar to the corresponding spectrum of the related neutral complex Pt(2-ppy)(ppy-N)Cl where ppy-N is the N-bound form of 2-phenylpyridine in which the 2'-carbon atom remains protonated. The electronic absorption spectrum of Pt(2-ppy)(ppy-N)Cl has absorption bands at 348 and 404 nm (ε_{max} = 1900 and 800 M⁻¹ cm⁻¹, respectively) that are assigned as MLCT transitions involving the 2-ppy chelate.²⁶ A related complex, Pt(2-ppy)₂, has absorption transitions at 402 and 484 nm (ε_{max} = 10400 and 90 M⁻¹ cm⁻¹, respectively) that are assigned as the ¹MLCT and ³MLCT transitions, respectively.⁵⁴ These transitions disappear when the complex is oxidized to the Pt(IV) species, Pt(2-ppy)₂Cl(CH₂Cl), supporting the MLCT assignment.¹⁶ It is thus logical to assign the strongly allowed band at 380 nm (ε_{max} = 9100 M⁻¹ cm⁻¹) and the band at 425 nm (ε_{max} = 450 M⁻¹ cm⁻¹) as the corresponding ¹MLCT and ³MLCT transitions in **4**.

Pt(2-ppy)(Et₂dtc) (**4**) luminesces at room temperature in solution, as shown in Figure 9. If a fluid solution of **4** is used to prepare a glassy matrix at 77 K, an emission spectrum of structure similar to, but at higher energy (~20 nm) than, that of the solid is observed. Emission spectra of the solid sample and the solvated

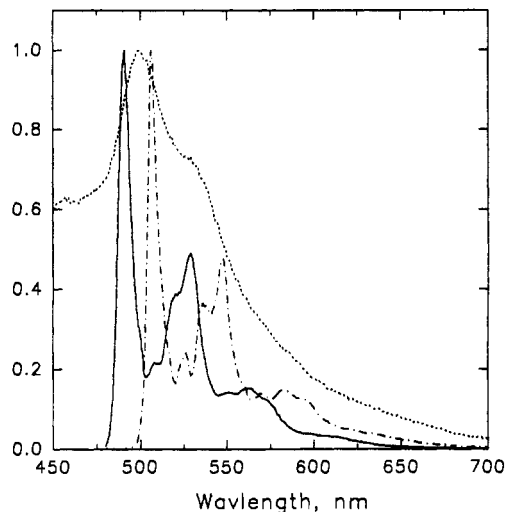


Figure 9. Emission spectra of Pt(2-ppy)(Et₂dtc) (**4**) at room temperature (- - -) (methylene chloride solution) and at 77 K in PRP glass (—) and in the solid state (- · -).

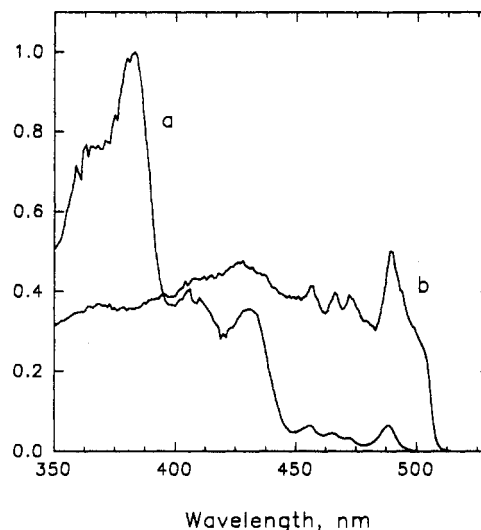


Figure 10. Excitation spectra of Pt(2-ppy)(Et₂dtc) (**4**) at 77 K in (a) PRP glass and (b) the solid state.

sample in rigid glass are also shown in Figure 9. The structure noted in the emission spectra of **4** are common to cyclometalated 2-phenylpyridine complexes of Pt(II), Pt(IV), Pd(II), Rh(III), and Ir(III).^{9-13,49-55} The λ_{max} of **4** at 77 K in PRP glass is 492 nm, which is nearly identical to the corresponding value of 491 nm for Pt(2-ppy)₂.¹⁰ The excitation spectra are also similar between **4** and Pt(2-ppy)₂. Excitation spectra of **4** are illustrated in Figure 10. The excitation spectrum of **4** in rigid glass displays features similar to those observed in the solution absorption spectrum. Similar spectral features are observed in the solid state excitation spectrum.

The emission spectrum of **4** in PRP glass at 77 K (Figure 10) exhibits a vibrational structure that is typical of emission from

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ligand-centered (LC) or MLCT excited states.⁵⁶ Comparison with the emission spectrum of the C-protonated neutral ligand shows that the emission bands of the complex are red-shifted by $\sim 3000\text{ cm}^{-1}$. Also, the structures of the emission are very different between the complexed and uncomplexed ligand. These results are taken as supportive of a MLCT emitting state involving the 2-phpy chelate for complex 4, although a ligand centered state with some metal character cannot be completely ruled out.

Conclusions

Pt(diimine)(dithiolate) complexes, related cationic diethyldithiocarbamate derivatives, and Pt(2-phpy)(Et₂dtc) were synthesized to examine their emission behavior and to probe the effect of ligand charge on their luminescence. The structures of two *cis*-1,2-dicarbomethoxyethylene-1,2-dithiolate (met) complexes were established by single crystal X-ray structure determinations to be square planar with minor deviations from the idealized geometry. The complexes containing a diimine chelate and either a dithiolate or a dithiocarbamate chelate have a solvatochromic absorption band assigned as a (Pt(d)/S(p)- π^* _{diimine}) charge transfer. All of the complexes containing diimine

chelates or the α -C-deprotonated form of 2-phenylpyridine are emissive in fluid solution. On the basis of the emission results and comparison with other emissive dithiolate complexes, the following emissive states are assigned: (a) Pt(Ph₂phen)(tbcda) (1), Pt(Ph₂phen)(cpdt) (2), and Pt(Me₂bpy)(Et₂dtc)⁺ (3) possess multiple emitting states, including a $^3(\pi-\pi^*$ _{diimine}) intraligand state of the diimine ligand and a triplet state having the same orbital parentage as the solvatochromic transition; (b) Pt(Me₂bpy)(met) (5), Pt(COD)(met) (6), and Pt(P(OMe)₃)₂(met) (7) have a single emitting state which is assigned as $^3(\text{Pt(d)}/\text{S(p)}-\pi^*$ _{dithiolate}); (c) the excited state of Pt(2-phpy)(Et₂dtc) (4) is assigned to a metal-to-ligand charge transfer involving the 2-phenylpyridine chelate.

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Supplementary Material Available: Complete listings of crystallographic details, bond lengths, bond angles, calculated H atom positional parameters, and anisotropic thermal parameters for Pt(Me₂bpy)(met) (5) and Pt(P(OMe)₃)₂(met) (7) (11 pages). Ordering information is given on any current masthead page.

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