

STRUCTURE, SPECTROSCOPY AND PHOTOCHEMISTRY OF PLATINUM(II)
DIIMINE COMPLEXES

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Abstract

Platinum(II) bipyridyl complexes exhibit rich absorption and emission properties in the solid and solution states, which can be understood within the context of their electronic and molecular structures. Depending on the ancillary ligands, the emission from square planar monomers originates from either an intraligand $\pi \rightarrow \pi^*$, ligand field, or MLCT triplet state. Tuning the electron-donating properties of a series of pyrazolate ligands induces energy crossover between the lowest $^3\pi \rightarrow \pi^*$ and $^3\text{MLCT}$ states.

The Pt...Pt distances determined by X-ray crystallography for nine linear-chain platinum(II) diimine complexes range from 3.24 to 3.49 Å. While we find evidence for interligand interactions influencing these structures, the Pt...Pt bonds are the most important stacking forces. The metal-metal distances are consistent with an electronic structural model in which σ -donor / π -acceptor ligands strengthen Pt...Pt bonding interactions. The intense colors of the linear-chain solids and related binuclear complexes (orange, red, violet, or blue) are due to an electronic transition to the $^1\text{MLCT}[\text{d}\sigma^*(\text{Pt}) \rightarrow \pi^*(\text{diimine})]$ state, where the HOMO ($\text{d}\sigma^*$) derives from the interaction of the fully occupied 5d_{z^2} levels of adjacent Pt centers and the LUMO (π^*) is predominantly centered on the diimine ligand. The intense emission from these materials originates from the corresponding $^3\text{MLCT}$ state. Overall, the emission and absorption spectra are consistent with an electronic structural model that accounts for the electronic properties of the ancillary ligands, as well as the Pt...Pt interactions. Interestingly, for the red form of $\text{Pt}(\text{bpy})\text{Cl}_2$ (bpy=2,2'-bipyridine) the Pt...Pt distance shortens from 3.449(1) to 3.370(2) Å in the interval between 294 and 20 K. The emission maximum red-shifts as the temperature drops (613 nm, 300 K; 651 nm, 10 K), with the peak energy decreasing linearly with the inverse cube of the Pt...Pt separation.

The violet color of $\text{Pt}(\text{bpy})(\text{bdt})$ (bdt=1,2-benzenedithiolate) is due to a low-energy transition to a metal-mixed ligand-to-ligand charge-transfer state (LLCT); the emission originates from the corresponding triplet state. Photochemical oxidation of

Pt(bpy)(bdt) occurs in the presence of oxygen; this reaction has been investigated by ^1H NMR and UV-visible absorption spectroscopy, as well as transient absorption spectroscopy. Singlet oxygen produced by energy transfer from the excited complex is implicated as the active oxygen species, in sequential formation of the sulfinic and disulfinate products. Both products have been characterized by X-ray crystallography.

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List of Abbreviations and Symbols

bph	biphenyl dianion
bpm	2,2'-bipyrimidine
bdt	1,2-benzenedithiolate
bpy	2,2'-bipyridine
dmbpy	4,4'-dimethyl-2,2'-bipyridine
dmf	<i>N,N</i> -dimethylformamide
dmpzH	3,5-dimethylpyrazole
dmsO	dimethylsulfoxide
ϵ	extinction coefficient ($\text{M}^{-1}\text{cm}^{-1}$)
EMD	10:10:1 ethanol:methanol: <i>N,N</i> -dimethylformamide
en	ethylenediamine
EPR	electron paramagnetic resonance
ET	electron transfer
EXAFS	extended X-ray absorption fine structure
fwhm	full width at half maximum
g	gram
HOMO	highest occupied molecular orbital
<i>i</i> -biq	3,3'-biisoquinoline
LF	ligand field
LUMO	lowest unoccupied molecular orbital
mnt	maleonitriledithiolate
meimidSH	2-mercapto-1-methyl-imidazole
MeT	deprotonated 1-methylthymine
MeU	deprotonated 1-methyluracil
ml	milliliter
MLCT	metal-to-ligand charge-transfer

NHE	normal hydrogen electrode
nmp	1-methyl-2-pyrrolidinone
NMR	nuclear magnetic resonance
phen	1,10-phenanthroline
pySH	2-mercaptopyridine
pzH	pyrazole
s	second
SCE	saturated calomel electrode
tdt	3,4-toluenedithiolate
tmpzH	3,4,5-trimethylpyrazole

Chapter 1

Introduction

The thermal and photochemical reactivity of molecules is a direct consequence of their electronic and three-dimensional structures. Since transition metal complexes have many practical applications, including catalysis, chemical sensing and materials engineering, considerable effort has been devoted to understanding the factors governing their electronic and molecular structures, both in the ground and excited states. The central premise of these investigations is that, with this knowledge, molecules exhibiting desirable chemical and physical properties can be rationally engineered.

In this regard, a long-standing goal for chemists has been to utilize light energy to drive thermodynamically or kinetically unfavorable reactions.¹⁻⁵ The energy, structure and electronic distribution for a molecule in an excited state can be very different from the ground state. For example, in an excited state a molecule is both a better oxidant and reductant than in the ground state. Therefore, if the excited state is sufficiently long lived, the enhanced reactivity may be harnessed in an electron-transfer or other chemical reaction. The photosynthetic process that converts solar energy to chemical energy in the form of ATP (adenosine triphosphate) and NADPH (nicotinamide adenine dinucleotide phosphoric acid) for the eventual reduction of CO₂ is one of the most important examples of this reactivity.^{6,7} Before chemists can match the remarkable efficiency of biological photosynthesis in artificial systems, a detailed understanding of energy-transfer and electron-transfer reactions is necessary. Our studies are motivated by the fact that these reactions depend directly on the electronic properties and static and dynamic structure of molecules. Since the electronic and molecular structure are inextricably interrelated, we require a fundamental understanding of the relationship between electronic structure, molecular geometry and intermolecular interactions. With this goal in mind, we embarked on a detailed study of platinum(II) diimine complexes. Our strategy combined spectroscopic techniques for

the investigation of electronic structure and X-ray crystallography for the elucidation of molecular structure and intermolecular interactions.

Our interest in platinum(II) diimine compounds is, in part, driven by the possibility of coupling desirable characteristics of Pt complexes with photophysical properties of transition metal diimine complexes. The tendency of platinum complexes to favor thermal multielectron reactions over single-electron processes⁸ suggests that they also may be amenable to photoinduced multielectron transfer chemistry. Indeed, many of the most important targets in photochemistry today involve multiple electron-transfer processes (*e.g.*, conversion of water to H₂ and O₂, C-H bond activation, nitrogen fixation). In addition, square planar platinum(II) complexes offer the possibility for metal-assisted reactions *via* direct substrate-Pt interaction at the open coordination sites of the complex. Furthermore, since transition metal complexes with diimine ligands such as⁹⁻¹¹ Ru(bpy)₃²⁺ and¹²⁻¹⁴ Re(phen)(CO)₃L⁺ (bpy=2,2'-bipyridine; phen=1,10-phenanthroline) often exhibit long-lived metal-to-ligand charge-transfer (MLCT) excited states in fluid solution, it is logical to combine these ligands with Pt to obtain photoactive complexes.

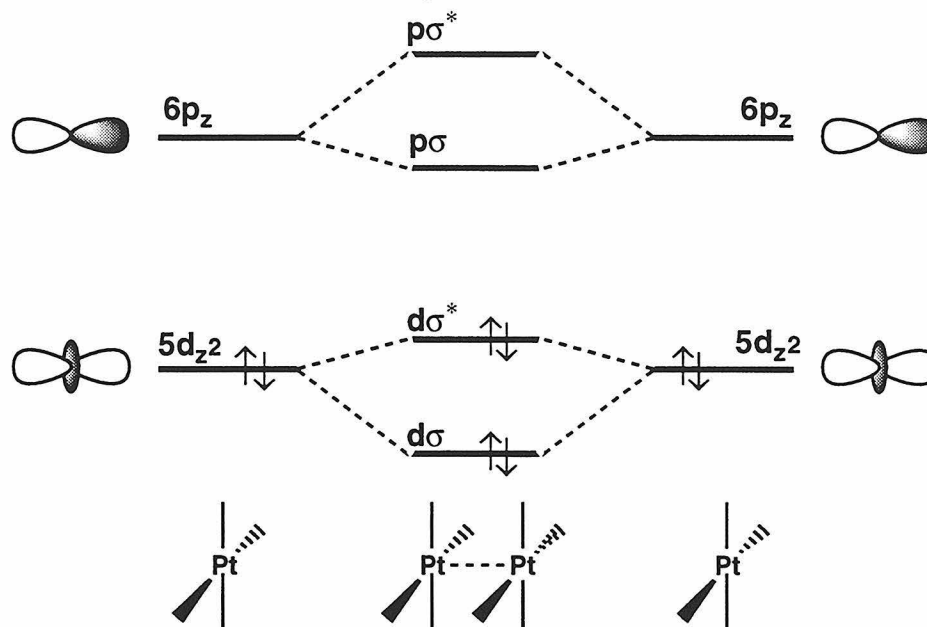
In fact, platinum(II) diimine complexes (*e.g.*, Pt(diimine)L₂) often show intense green to red emission in glassy solution and solid-state forms. In the case of innocent ligands (L), that is, ligands that do not participate in the observed electronic transitions, the emissive state is usually an intraligand $\pi \rightarrow \pi^*$ or ligand field (LF) triplet state.^{15,16} Generally, for compounds containing exclusively strong-field ligands (*e.g.*, Pt(bpy)(en)²⁺, en=ethylenediammine) the lowest excited state is predominantly ligand-centered and gives rise to a highly structured green emission. On the other hand, for complexes with weak-field ancillary ligands (*e.g.*, Pt(bpy)Cl₂), a characteristic broad red emission originates from a lowest ³LF state.¹⁷ In some instances, solid-state or solution intermolecular interactions involving the diimine ligand can result in excimer emission.^{16,18-20} While the existence of low-lying $^3\pi \rightarrow \pi^*$ and ³LF states strongly

suggests the presence of a nearby $^3\text{MLCT}$ state, an earlier study by Miskowski and Houlding¹⁶ found no evidence of $^3\text{MLCT}$ emission from platinum(II) bipyridyl complexes with innocent ligands.

An intriguing situation arises when non-innocent ligands, such as dithiolates, are integrated into the Pt(diimine) complex. Since the lowest unoccupied molecular orbital (LUMO) of platinum(II) diimine complexes is often the ligand-centered π^* level of the diimine,²¹⁻²⁴ binding of a strongly reducing bidentate ligand opposite the diimine results in a donor-acceptor type complex. Because it is the ligands that assume the roles of donor (dithiolate) and acceptor (diimine) and the metal that acts as the bridge mediating electronic coupling, these molecules share a converse relationship with asymmetric mixed-valence complexes (*e.g.*, $(\text{CN})_5\text{Ru}^{\text{II}}(\text{CN})\text{Ru}^{\text{III}}(\text{NH}_3)_5$)^{25,26} popularized in studies of electron transfer.²⁷⁻³⁰ Platinum(II) diimine dithiolate complexes are intensely colored because of a low-energy absorption commonly referred to as a ligand-to-ligand charge-transfer (LLCT) transition, involving oxidation of the dithiolate with concomitant reduction of the diimine. Recently, these complexes have received considerable attention,³¹⁻³⁵ because they often exhibit luminescence from the long-lived triplet LLCT excited state in room-temperature fluid solution.^{36,37} Eisenberg and co-workers³¹⁻³⁵ have suggested that a more accurate assignment is the $^3\text{d}(\text{Pt})/\text{p}(\text{S})\pi \rightarrow \pi^*(\text{diimine})$ state, where the HOMO derives from a mixture of Pt and S orbitals, emphasizing the role of the metal in electronic coupling. Interestingly, Pt(diimine)(dithiolate) complexes have been shown to undergo a variety of photochemical reactions that have yet to be fully characterized.^{31,32,38-41}

Another intriguing characteristic of square planar d^8 electron complexes is their propensity to form face-to-face dimers, oligomers and linear-chain materials with short metal-metal contacts ($<3.5 \text{ \AA}$).^{42,43} In this configuration, the orbitals of the adjacent metal centers strongly interact. The fully occupied 5d_{z^2} levels split to give bonding ($\text{d}\sigma$) and antibonding ($\text{d}\sigma^*$) molecular orbitals; similarly, the unoccupied 6p_z levels split to

give $p\sigma$ and $p\sigma^*$ orbitals. Since both the $d\sigma^*$ and $d\sigma$ levels are fully occupied, no formal Pt-Pt bonding occurs. However, configuration interaction with the $p\sigma$ and $p\sigma^*$ orbitals stabilizes the $d\sigma^*$ and $d\sigma$ levels, resulting in net favorable interactions.⁴⁴



These interactions lead to striking spectroscopic and photophysical properties. The lowest energy electronic transition involves excitation of an electron from an antibonding $d\sigma^*$ orbital (d_{z^2} parentage) to a bonding $p\sigma$ orbital (p_z parentage). In the cases of dimers, the resulting $^3d\sigma^* \rightarrow p\sigma$ excited state is frequently long-lived in fluid solution. Consequently, the binuclear complexes exhibit rich photochemistry that includes electron-transfer and atom-transfer reactions.^{11,45-52} Surprisingly, there are few examples of binuclear platinum(II) diimine complexes, and their spectroscopy has not been closely examined.⁵³⁻⁵⁸

In contrast, linear-chain platinum(II) diimine complexes are well known, including neutral stacks (*e.g.*, $\text{Pt}(\text{bpy})(\text{Cl})_2$, $\text{Pt} \cdots \text{Pt}$ 3.448(1) Å)⁵⁹ and double salts (*e.g.*, $[\text{Pt}(\text{bpy})(\text{en})][\text{Pt}(\text{CN})_4]$, $\text{Pt} \cdots \text{Pt}$ ~3.3 Å).⁶⁰ Studies of the spectroscopic and photophysical properties of these materials have established that the electronic structures of platinum(II) diimine complexes are strongly perturbed by solid-state effects, such as $\text{Pt} \cdots \text{Pt}$ and ligand $\cdots$ ligand intermolecular interactions.^{16,17,60-62} While

these complexes typically dissolve to give yellow or colorless solutions, they can form deeply colored solids (orange, red, violet, and blue) that are intensely luminescent at room temperature. Recently, these materials have attracted interest, in part, because certain water insoluble platinum(II) salts containing bipyridyl ligands (*e.g.*, [Pt(bpy)₂][Pt(CN)₄]) have been shown to undergo photoinitiated ($\lambda > 400$ nm) multielectron transfer, sensitizing the production of hydrogen from water. In addition, Mann and co-workers⁶³ have exploited the vapor sensitivity of the spectroscopy of related linear-chain compounds in chemical sensing applications. The properties of the platinum(II) diimine systems indicate that the presence of the low-lying diimine π^* level results in a somewhat different lowest excited state, namely a $^3d\sigma^* \rightarrow \pi^*$ state;^{16,17,60} however, we note that there is still some debate surrounding this assignment.⁶⁴⁻⁶⁷ Unfortunately, while many these materials have been prepared, the absence of structural information has, in most cases, limited interpretation of their spectroscopic properties.

A central goal in materials science is the controlled assembly of molecules to prepare solids with desirable properties. By engineering highly organized molecular arrays, it should be possible to exploit molecular electronic and structural anisotropy, as well as intermolecular interactions, to prepare materials with highly anisotropic properties that are vastly different from those of amorphous solids. Crystals composed of stacked platinum(II) complexes forming linear-chain structures are prominent examples of such materials. The chief component that is missing from most current methodologies for preparing novel materials is the element of molecular control. A strategy based on mainly empirical methods (“shake and bake” chemistry) is still the most widely employed, as emphasized by the rising popularity of combinatorial approaches.^{68,69} Along with steric factors, such as molecular shape, *intermolecular* electronic interactions are a fundamental factor dictating the organization of molecules in solids. These considerations are, in part, the underlying motivation for our investigations of the

electronic structures of stacked platinum(II) complexes. In analogy to hydrogen bonds in crystal engineering, intermolecular interactions between d^8 metal centers provide a potentially powerful tool for the controlled assembly of molecules. Therefore, there is strong motivation to compile a structural and spectroscopic database for a series of these compounds in order to elucidate the factors governing their stacking interactions and resulting electronic structures.

Before examining the linear-chain complexes or the diimine dithiolate system, we set out to solidify our understanding of the lowest excited-state structure of $\text{Pt}(\text{diimine})\text{L}_2^{2+}$ monomers. To this end, Chapter 2 details a strategy for tuning a lowest MLCT excited state. This approach emphasizes strong-field ancillary ligands that destabilize the lowest $d \rightarrow d$ excited states. The electron-donor properties of these ligands are an equally important consideration, since strongly electron-donating ligands, such as pyrazolates, tend to stabilize the MLCT states of these complexes. By tuning the electron-donating properties of a series of pyrazolate ligands, an energy crossover between the lowest $^3\pi \rightarrow \pi^*$ and $^3\text{MLCT}$ states is achieved, thus changing the nature of the emissive state.

In Chapters 3-5, we turn our attention to $\text{Pt} \cdots \text{Pt}$ interactions. In the spirit of the Structure Correlation principle of Bürgi and Dunitz,⁷⁰ Chapter 3 details an analysis of the structures of nine neutral linear-chain platinum diimine complexes ($\text{Pt} \cdots \text{Pt}$, 3.24-3.49 Å) and an electronic model describing the stacking interactions is presented. In Chapter 4, we examine the spectroscopy of these linear-chain complexes and establish that the emission from these materials originates from a lowest $^3d\sigma^* \rightarrow \pi^*$ state. The emission and absorption spectroscopy of these materials is consistent with an electronic structural model that considers the properties of the ancillary ligands, as well as variations in the $\text{Pt} \cdots \text{Pt}$ separations. In Chapter 5, we extend our studies of d^8 - d^8 interactions to bridged-binuclear complexes. The $^3d\sigma^* \rightarrow \pi^*$ state also is the emissive state in these compounds.

Interestingly, we have encountered some unusual structural isomerism when using 2-mercaptopyridinate as a bridging ligand.

Chapter 6 is devoted to the study of a single complex, namely Pt(bpy)(bdt) (bdt=1,2-benzenedithiolate). Our data support an interpretation of the LLCT state in terms of semi-classical electron-transfer theory, and this state is described as a metal-mixed LLCT state. We also have extensively examined the photoreaction of Pt(bpy)(bdt) with oxygen, and for the first time, the photoproducts have been identified. The reaction involves conversion of the dithiolate to the sulfinato and disulfinato species in sequential steps. Singlet oxygen sensitized by the excited Pt complex is implicated as the active oxidizing agent. Interestingly, the transient absorption spectra are consistent with generation of a persulfoxide intermediate or superoxide. These results lead to the suggestion that this and related chromophores could be used as mechanistic model systems for singlet oxygen activation of organic sulfides.

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Chapter 2

Tuning the Excited States of Platinum(II) Bipyridyl Complexes

I. Introduction

One of the most striking characteristics of square planar platinum(II) diimine compounds is their broad range of colors. For example, in solution complexes with innocent ancillary ligands (*e.g.*, Cl^- or NH_3) are typically yellow or colorless. In contrast, stacked complexes with short Pt $\cdots$ Pt contacts ($<3.5 \text{ \AA}$) or complexes with easily oxidized ligands (*e.g.*, dithiolates) may be intensely colored (orange, red, violet or blue). Understanding the origin of these dramatic color variations is a profoundly intriguing problem for physical inorganic chemists using the tools of molecular spectroscopy. Before tackling the cases involving intermolecular interactions (Chapters 4 and 5) or dithiolate ligands (Chapter 6), a firm grasp of the electronic structure of platinum(II) diimine monomers is required. In this chapter, the spectroscopic and photophysical properties a series of platinum(II) bipyridyl complexes are described. In one instance, we detail the effect of ligand field strength on the spectroscopy of three bis(halo) complexes, $\text{Pt}(\text{bpy})\text{X}_2$ (bpy=2,2'-bipyridine; $\text{X} = \text{Cl}, \text{Br}, \text{I}$), and draw on these trends to assign the lowest energy feature in the absorption spectrum of $\text{Pt}(\text{bpy})\text{Cl}_2$. In a second series of complexes with derivatized pyrazolate ligands, the electronic properties of the ancillary pyrazolate ligands are used to tune the nature of the emissive state.

A. Electronic Structure

Platinum(II) diimine complexes often exhibit intense green to red emission in glassy solution and solid-state forms. This luminescence is diagnostic of the lower excited-state electronic structure. In the case of innocent ligands, the emissive state may be either an intraligand $\pi \rightarrow \pi^*$, ligand field (LF), or metal-to-ligand charge-transfer (MLCT) triplet state.¹ Thus, for compounds containing exclusively strong-field ligands (*e.g.*, $\text{Pt}(\text{bpy})(\text{en})^{2+}$, en=ethylenediammine) the lowest excited state is predominantly ligand-centered and gives rise to a highly structured green emission. On the other hand, for complexes with weak-field ancillary ligands (*e.g.*, $\text{Pt}(\text{bpy})\text{Cl}_2$), a characteristic broad

red emission originates from a lowest ^3LF state.² The electronic structure is readily described using the molecular orbital diagram in Figure 2.1. Listed in Table 2.1 are a series of platinum(II) bipyridyl complexes along with their solid-state photophysical properties;² these data are useful to consider during the following discussion.

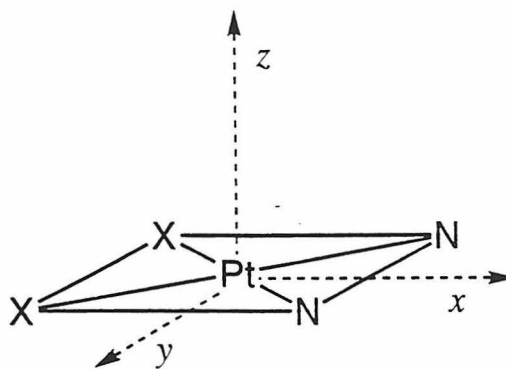
Table 2.1. Photophysical properties of some platinum(II) bipyridyl complexes in the solid state.²

Compound (color)	Room Temperature Emission Maxima (nm)	Lifetime (μs)	Emissive State
[Pt(bpy)(en)](ClO ₄) ₂ (yellow)	461, 482sh, 492, 521, 530sh, 569sh, 607sh	1.4	$^3\pi \rightarrow \pi^*$
Pt(dmbpy)(CN) ₂ (yellow)	455, 488, 518, 557, 600sh	1.82	$^3\pi \rightarrow \pi^*$
Pt(bpy)Cl ₂ (yellow)	(624, 77K) (630, 10K)	(23) (3.4)	^3LF
Pt(dmbpy)Cl ₂ (yellow)	645 (647, 10K)	1.24 (5.1)	^3LF
Pt(3,3'-(CO ₂ Me) ₂ bpy)Cl ₂ (orange)	550sh, 595 (555, 595, 645sh, 10K)	0.35 (1.1)	$^3\text{MLCT}$

The possibility of a lowest energy Pt(d $\rightarrow$ p) or ligand-to-metal charge-transfer (LMCT) state can be rejected on energetic grounds. Vibronic structure associated with the lowest energy triplet intraligand $\pi \rightarrow \pi^*$ transition in platinum bipyridyl complexes originates near 450 nm. However, the lowest energy d $\rightarrow$ p transitions in platinum(II) complexes typically occur at wavelengths shorter than 250 nm. For example, the d_{z²} $\rightarrow$ p_z transitions to the E_u($^3\text{A}_{2u}$) state (D_{4h} symmetry with spin-orbit coupling) of [Pt(NH₃)₄]²⁺ and [PtCl₄]²⁻ occur at <220 nm.³⁻⁶ Similarly, even in the extreme weak-field case of PtCl₄²⁻ with high energy anionic ligand orbitals, the energy of the lowest E_u($^3\text{B}_{1u}$) LMCT[d_{xy} $\rightarrow$ p_z] state is greater than 42000 cm⁻¹ (<240 nm).⁴

Figure 2.1 (a) Coordinate system used in the discussion of square planar MN_2X_2 complexes. (b) Qualitative molecular orbital diagram for platinum(II) bipyridyl complexes. The diagram includes the molecular orbitals referenced in text and their C_{2v} symmetry labels. (D_{4h} symmetry labels for relevant orbitals are shown in parentheses.) For the ordering indicated, the lowest energy electronic transition is from the $d_{x^2-y^2}$ level to the antibonding d_{xy} level. A limitation of this one-electron description becomes apparent if one considers the vastly different singlet-triplet splittings for the $\pi \rightarrow \pi^*$ ($\sim 9000 \text{ cm}^{-1}$) and MLCT ($\sim 3000 \text{ cm}^{-1}$) states. Consequently, this discussion emphasizes the energies of states rather than the energies of orbitals.

(a)



(b)

 C_{2v} (D_{4h}) a_2 ————— $\pi_2^*(\text{bpy})$ b_1 ————— p_z (a_{2u}) b_1 ————— $\pi^*(\text{bpy})$ b_2 ————— d_{xy} (b_{2g})

b_1	$\uparrow\downarrow$	d_{xz}	} (e_g)
a_2	$\uparrow\downarrow$	d_{yz}	

 a_2 $\uparrow\downarrow$ $\pi(\text{bpy})$ a_1 $\uparrow\downarrow$ $d_{x^2-y^2}$ (b_{1g}) a_1 $\uparrow\downarrow$ d_{z^2} (a_{1g})

B. Electronic Transitions

1. $\pi \rightarrow \pi^*$ Transitions

Emission from $^3\pi \rightarrow \pi^*$ states in metal complexes can be identified by comparison with spectra of the free ligand^{7,8} or other diimine complexes.^{9,10} One major drawback to the first approach is that the free ligand geometry is not likely to be planar. In addition, the electronic effects of coordinated nitrogen lone-pairs are more likely to resemble those in another complex rather than those in the free diimine. For these reasons, coordination complexes such as $\text{Zn}(\text{bpy})_3^{2+}$ and $\text{Ir}(\text{bpy})_3^{3+}$ are more suitable model systems. The zinc d^{10} system is free of low-lying ligand field and charge-transfer bands, and the lowest excited state in the iridium system has been confirmed to be a $^3\pi \rightarrow \pi^*$ state.¹⁰

The absorption spectra of platinum(II) bipyridyl complexes exhibit characteristic intense structure originating in the 300-325 nm region and tailing off to shorter wavelengths with spacings of $\sim 1000\text{-}1500\text{ cm}^{-1}$. These features correspond to vibronic structure of an intraligand $^3\pi \rightarrow \pi^*$ transition and are similar to the progression originating at 309 nm in the spectrum of $\text{Zn}(\text{bpy})_3^{2+}$.^{7,8} In some instances, the spin-forbidden $^3\pi \rightarrow \pi^*$ transition near 450 nm is resolved (*e.g.*, $\text{Pt}(\text{bpy})(\text{en})^{2+}$, 447 nm, $\epsilon\ 6\text{ M}^{-1}\text{cm}^{-1}$; $\text{Pt}(\text{dmbpy})(\text{CN})_2$, $\text{dmbpy}=4,4'\text{-dimethyl-}2,2'\text{-bipyridine}$).^{11,12} This progression is not found in the $\text{Zn}(\text{bpy})_3^{2+}$ spectrum and is probably amplified by heavy-atom spin-orbit coupling in the platinum(II) bipyridyl and $\text{Ir}(\text{bpy})_3^{3+}$ (450 nm, $\epsilon\ 10$) spectra.⁷⁻¹⁰ The singlet-triplet splitting is very large ($\sim 9000\text{ cm}^{-1}$) and the energies of these states are relatively constant from complex to complex. In solution, $\text{Pt}(\text{bpy})\text{Cl}_2$ exhibits a lowest energy absorption at $\sim 475\text{ nm}$ that has been attributed to either a low-lying triplet $^3\pi \rightarrow \pi^*$ or $d \rightarrow d$ band.¹¹ In this chapter, we examine this transition in more detail using diffuse reflectance and single-crystal polarized absorption.

At room temperature, the green emission from the $^3\pi \rightarrow \pi^*$ state is usually structured for both solid-state and solution samples. The Stokes shift is generally small, and the radiative rate constant (k_r) is on the order of 10^4 s^{-1} .^{2,11-14} For example, the first

band at 458 nm in the structured emission from samples of $[\text{Pt}(\text{bpy})(\text{en})](\text{ClO}_4)_2$ overlaps the $^3\pi \rightarrow \pi^*$ absorption at 447 nm.¹¹ The vibronic pattern is nearly identical with the $\text{Zn}(\text{bpy})_3^{2+}$ emission, and the radiative rate constant is $5.3 \times 10^4 \text{ s}^{-1}$.^{7,8,11}

In some cases (*e.g.*, $[\text{Pt}(\text{phen})_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ and $[\text{Pt}(\text{bpy})_2](\text{ClO}_4)_2$), solid-state interactions of diimine ligands in adjacent complexes may result in excimer emission. These broad structureless bands occur at lower energy than their monomer counterparts.^{11,15} Excimer emission may also occur in solution (*e.g.*, $\text{Pt}(4,4'\text{-di-tert-butyl-2,2'-bipyridine})(\text{CN})_2$ and $\text{Pt}(4,7\text{-diphenyl-phenanthroline})(\text{CN})_2$).^{16,17} At low concentrations, the monomer emission dominates the spectrum. However, as the concentration is increased, the excimer band grows in relative intensity.

2. $d \rightarrow d$ Transitions

The lowest spin-forbidden ligand field absorption for $\text{Pt}(\text{NH}_3)_4^{2+}$ occurs at 289 nm.⁵ Thus, in the strong-field case, the $^3\pi \rightarrow \pi^*$ states of the diimine complex are expected to lie well below the ligand field states. However, weaker fields may substantially lower the energy of $d \rightarrow d$ transitions. For $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, $\text{Pt}(\text{pyridine})_2\text{Cl}_2$ and $\text{Pt}(\text{en})\text{Cl}_2$, the lowest observed ligand field spin-forbidden transitions (3A_2 , 3B_1 ; d_{xz} , $d_{yz} \rightarrow d_{xy}$) occur at 422 nm, 455 nm, and (3B_2 ; $d_{x^2-y^2} \rightarrow d_{xy}$) 402 nm, respectively; and the corresponding spin-allowed transitions (1A_2 , 1B_1) occur at 308 nm, 370 nm, and (1B_2) 301 nm.¹⁸⁻²² (As in Figure 2.1a, z is perpendicular to the molecular plane and x lies along the C_2 molecular symmetry axis.) Consequently, in the weak-field case, LF states of $\text{Pt}(\text{diimine})(\text{X})_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) may lie below the $^3\pi \rightarrow \pi^*$ states.

The red ligand field emission from $\text{Pt}(\text{diimine})\text{Cl}_2$ complexes is characteristically broad (full width at half maximum = fwhm $\sim 3000\text{--}4000 \text{ cm}^{-1}$) with a large Stokes shift ($\sim 3000\text{--}4000 \text{ cm}^{-1}$) between the lowest energy absorption feature and the emission maximum. These features suggest a large excited-state distortion resulting from the population of the antibonding $d_{xy}(b_2)$ level.^{11,23} Even for the *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ in a 77 K

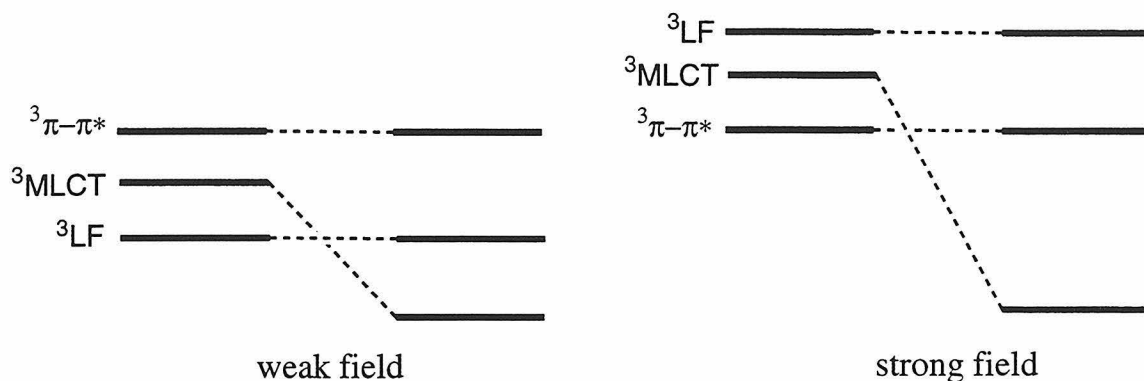
glass, the emission maximum occurs at 590 nm (Stokes shift of $\sim 6750\text{ cm}^{-1}$) with a fwhm of 3500 cm^{-1} .¹⁸ Pt(phen)Cl₂, Pt(bpy)Cl₂ and Pt(dmbpy)Cl₂ exhibit temperature independent emission (λ_{max} : 624, 630 and 645 nm) similar to that of *cis*-Pt(NH₃)₂Cl₂. All three emission bands are characteristically broad (fwhm: 3700, 3300 and 2700 cm^{-1} , respectively) and strongly shifted to lower energy from the estimated position of the lowest Pt(diimine)Cl₂ ³LF absorption (500-550 nm). For Pt(dmbpy)Cl₂, the radiative rate constant is 5100 s^{-1} ;^{2,11} since the d→d transitions are Laporte forbidden, k_{r} is typically an order of magnitude smaller than that observed for $^3\pi\rightarrow\pi^*$ emission.^{11,23}

3. MLCT Transitions

MLCT absorption is more difficult to identify than either the intraligand or LF transitions. Though more intense than the d-d bands, MLCT absorption features can be easily obscured by $\pi\rightarrow\pi^*$ vibronic structure. However, in contrast to intraligand and d→d transitions, MLCT absorption and emission is very solvent sensitive due to inequivalent interaction of solvent with the metal d and ligand π orbitals. Thus, solvent dependence has been used as criterion for assigning ¹MLCT absorption bands in Pt(bpy)X₂ (X= Cl, Br or I), and Pt(bpy)(alkyl)₂ complexes.^{24,25} (Because of this solvent sensitivity, care must be taken when comparing energies of MLCT states for different complexes.) Lowest ¹MLCT absorptions in platinum(II) complexes typically occur at short wavelengths. For example, the lowest MLCT bands in Pt(CN)₄²⁻, *cis*-Pt(CN)₂(NH₃)₂ and Pt(NH₃)₄²⁺ occur at 280, 244 and <200 nm, respectively.^{5,26} However, because of the low energy of the π^* levels of aromatic diimine ligands, Pt(II) diimine complexes often exhibit MLCT absorption features in the near UV region (300-400 nm); these transitions are best characterized as platinum-to-diimine charge-transfer transitions.

C. Tuning Excited States

While the existence of low-lying $^3\pi\rightarrow\pi^*$ and ^3LF states strongly suggests the presence of a nearby $^3\text{MLCT}$ state, an earlier study by Miskowski and Houlding¹¹ found no evidence of $^3\text{MLCT}$ emission from platinum(II) bipyridyl complexes with innocent ligands (*e.g.*, NH_3 and Cl^-). These authors have proposed two strategies^{23,27} that employ either strong or weak-field ligands to achieve a lowest $^3\text{MLCT}$ excited state:



In the weak-field case, electron-acceptor groups are introduced on the diimine ligand of a complex with weak-field ligands. In the strong-field case, strongly electron-donating ancillary ligands should destabilize the metal levels resulting in a lowest $^3\text{MLCT}$ state.

The efficacy of the first approach is demonstrated by the spectroscopy of $\text{Pt}(3,3'-(\text{CO}_2\text{Me})_2\text{bpy})\text{Cl}_2$. Because of the electron-withdrawing groups on the bipyridyl ligand, the lowest $^1\text{MLCT}$ absorption band for this compound (CH_2Cl_2 : 444 nm, ϵ 3030) is shifted by 2900 cm^{-1} to lower energy from that of $\text{Pt}(\text{bpy})\text{Cl}_2$ (394 nm). Moreover, unlike the LF emission from $\text{Pt}(\text{bpy})\text{Cl}_2$, the solid-state emission from $\text{Pt}(3,3'-(\text{CO}_2\text{Me})_2\text{bpy})\text{Cl}_2$ is distinctly asymmetric, appearing as a mirror-image of the absorption. This band also shows good overlap with the $^3\text{MLCT}$ absorption, observed as a shoulder at 525 nm (ϵ 120). In contrast to the LF emission from $\text{Pt}(\text{bpy})\text{Cl}_2$, the 10 K emission spectrum shows vibronic structure ($\Delta\nu\sim 1300\text{ cm}^{-1}$) characteristic of the bipyridyl vibrational modes. Thus, the emission originates from the $^3\text{MLCT}[\text{d}_{xz}\rightarrow\pi^*]$

state. Unfortunately, this compound is not luminescent in room temperature solution, precluding characterization of the emissive state in solution.²³

The stabilization of the MLCT states in $\text{Pt}(3,3'-(\text{CO}_2\text{Me})_2\text{bpy})\text{Cl}_2$ is attributable in part to the strong π -donor properties of the chloride ligands. Indeed, the $^1\text{MLCT}$ for $\text{Pt}(\text{bpy})\text{Cl}_2$ is red-shifted by $>1000\text{ cm}^{-1}$ from that of¹¹ $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ and $>4500\text{ cm}^{-1}$ from that of $\text{Pt}(\text{bpy})(\text{CN})_2$.²⁸ This observation leads directly to a second strategy for achieving a lowest $^3\text{MLCT}$ state; namely, use of strongly electron-donating ancillary ligands. It is well known that strong σ -donors, such as methyl, stabilize MLCT states; for example, the lowest $^1\text{MLCT}$ absorption for $\text{Pt}(\text{bpy})(\text{CH}_3)_2$ in dichloromethane occurs at 467 nm.²⁵ In fact, $^3\text{MLCT}$ emission has been reported for several alkyl and aryl platinum(II) diimine complexes.²⁹⁻³³ In the case of $\text{Pt}(\text{bpy})(\text{mesityl})_2$, the ancillary ligands are proposed to block the open metal-coordination sites allowing for reversible electrochemical generation of Pt(III).²⁹ Undoubtedly, the strong electron-donating ancillary ligands increase the overall electron density on the platinum, thereby stabilizing the MLCT state.

In this chapter, we demonstrate the second approach for achieving a lowest $^3\text{MLCT}$ state by preparing a series of luminescent platinum(II) bipyridyl complexes with derivatized pyrazolate ligands. We find that the emission originates from a $^3\pi \rightarrow \pi^*$ or $^3\text{MLCT}$ state depending on the electron-donating properties of the ancillary ligands.

II. Experimental

A. Materials and Methods

All reagents were obtained from Aldrich and used without further purification, unless specified. In most cases, tetrahydrofuran (thf) was distilled under argon from sodium and benzophenone prior to use, and dichloromethane was distilled under argon from CaH_2 . Spectroscopic grade methanol was supplied by Burdick and Johnson. Solution emission samples were typically freeze/pump/thaw cycled four times to give a

final pressure of less than 10^{-3} mTorr; for some steady-state measurements on samples with short-lived excited states, air-saturated or argon-saturated solutions (bubble-degassed for 10 minutes) were used. Room-temperature solution samples were contained in a 1 cm pathlength quartz cuvet; 77 K glassy solution were prepared by inserting a quartz EPR tube containing the solution into a quartz-tipped finger dewar. Solid-state emission samples were contained in a quartz EPR tube or a sealed quartz capillary tube; for low-temperature measurements, the sealed capillary tube was placed in a CTI 350CP closed-cycle He Refrigerator from Janis Research. Elemental analyses were carried out by Galbraith Laboratories Inc., or Mr. Fenton Harvey of Caltech. Mass spectra were obtained from the Caltech Mass Spectrometry Laboratory.

B. Instrumentation

^1H NMR spectra were obtained using a Bruker AM500 Spectrometer. UV-vis spectra were recorded using a Hewlett-Packard Diode Array 8452A Spectrotometer or a Cary-14 spectrometer upgraded by OLIS to include computer control. Emission spectra were recorded using three different systems. These have been described elsewhere,^{11,23,34,35} and we summarize the most important elements of their configurations below.

Emission and excitation spectra of 77 K glassy solutions (3:1 ethanol:methanol) were measured using light from a Hanovia 200 W Hg/Xe (emission) or 150 W Xe lamp as the excitation source. The light was wavelength-selected using a SPEX 1681B 0.22 m Minimate monochromator, subsequently passed through a PAR 125A light chopper (108 Hz) and focused on the sample by a pair of 90° off-axis parabolic mirrors. The emission was collected at 90°, focused into a SPEX 1780 0.5 m monochromator and detected with a Hamamatsu R955 photomultiplier tube (PMT); the signal was amplified with a PAR Model 186A lock-in amplifier interfaced with a 386-based PC. Appropriate emission cut-off filters were used to protect the detector from scattered excitation light. Software

developed by Dr. James A. Bailey (Caltech) was used for monochromator control and data analysis. Emission and excitation spectra were corrected using the following calibration data; the wavelength dependence of the PMT was proportioned against the response of a calibrated UV-enhanced silicon photodiode to the 150 W Xe lamp spectrum; excitation spectra were proportioned against the 150 W Xe lamp profile obtained from a standard Rhodamine 6G quantum counter.

Solid-state emission studies were carried out by Dr. Virginia H. Houlding of Bandgap Technology Corp. using a SPEX Ramalog Raman spectrometer. The 457.9 nm laser line of a Spectra Physics 2020 5W argon ion laser was used to excite the sample; the emitted light was dispersed with a SPEX 1404 double 1 m monochromator and detected using an RCA C31034M single-photon counting detector. Typically, incident intensity was reduced to the 2-200 $\mu\text{W cm}^{-2}$ range using neutral-density filters. These emission spectra were corrected for instrumental response.³⁶

Since in room-temperature fluid solution, the platinum(II) pyrazolate complexes are only weakly luminescent, excitation using a Hg or Hg/Xe lamp resulted in emission spectra with poor signal-to-noise. However, high quality emission data were obtained using the 441.6 nm line (~ 20 mW) from a He/Cd laser as an excitation source. The emission was collected at 90° and dispersed using a Spex 1403 0.85 m Double Spectrometer equipped with a cooled R955 Hamamatsu PMT and an ORTEC 9315 single-photon counter. These spectra were not corrected for instrumental response.

Excitation pulses for solution emission lifetimes³⁷ were generated using a Quanta-Ray Nd:YAG laser (second or third harmonics: 532 or 355 nm) or a Lambda Physik LPX210i XeCl excimer-pumped Lambda Physik FL3002 dye laser (PBBO, 396 nm). The emission was passed through a monochromator prior to detection using a R955 Hamamatsu PMT. Data were analyzed using least-squares fitting programs (KINFIT and DECON) written by Dr. Jay R. Winkler (Caltech). For solid-state emission lifetimes,¹¹ the sample was excited using the third harmonic (355 nm) of a Quanta-Ray DCR3

Nd:YAG laser. The beam was severely attenuated to avoid sample heating and artifacts; measurements were made with different excitation intensities to ensure that the emission intensity was linear with excitation intensity. The emitted light was passed through Schott KV non-fluorescing cutoff filters and detected using a R928 PMT.

C. Diffuse Reflectance Spectroscopy

Diffuse reflectance and single-crystal polarized absorption spectra were recorded using a home-built diode array spectrometer optimized for handling small crystalline samples. The detector and sources (Xe or tungsten filament lamps) were fitted with fiber-optic cables which allow for considerable flexibility in experimental design. For diffuse reflectance measurements, samples were diluted in MgSO_4 and thoroughly ground. The powder was placed on a glass slide and gently flattened with the blade of a spatula; best results were obtained using highly homogenous samples prepared in an exactly identical fashion as a MgSO_4 reference blank. The source beam was orthogonal to the glass slide and focused on the sample. The fiber optic cable leading to the detector was positioned at 45° to the source and to the glass slide. A sample of MgSO_4 was used as a reference blank.

D. Single-Crystal Measurements

The optical components used for the diffuse reflectance measurements were re-configured for the single-crystal measurements. The source beam was directed vertically into the end of the detector fiber optic cable approximately 18" away. Optical components and the sample were placed in the path of the probe light. A linear polarizer was placed after the source; appropriate filters also were used to attenuate certain spectral regions of the source to avoid saturating the detector. The sample holder consisted of a 0.5 cm nickel disk with a small laser-drilled aperture in the center (100 μm for $\text{Pd}(\text{bpy})\text{Cl}_2$ and 30 μm for $\text{Pt}(\text{bpy})\text{Cl}_2$) glued to a 1" diameter brass disk with a larger aperture (2 mm) in its center. The brass disk served chiefly as a support for the nickel

disk and was of the appropriate dimensions for insertion into a rotating stage that was positioned between source and detection fibers. The aperture of the nickel disk was chosen to be smaller than the width of the crystal. Thus, the nickel disk served to mask the crystal so that the probe light could only reach the detector by passing through the sample, preventing stray source light from reaching the detector. Polarization measurements were made with the crystal positioned between the source and detector fibers. The stage supporting the sample holder was rotated in order to align the crystal optical axes with the polarizer.

Prior to recording spectra, unit-cell dimensions for Pd(bpy)Cl₂ and Pt(bpy)Cl₂ were obtained from the setting angles of 12 reflections using an Enraf-Nonius CAD4 diffractometer (Mo K_α radiation). Observed [previously reported] for orthorhombic Pd(bpy)Cl₂:³⁸ *a*, 18.257(14) [18.144(5)]; *b*, 15.861(12) [15.952(5)]; *c*, 7.483(9) Å [7.494(2)]. Observed [previously reported] for orthorhombic Pt(bpy)Cl₂:³⁸ *a*, 18.271(44) [18.257(4)]; *b*, 15.754(28) [15.795(3)]; *c*, 7.467(32) Å [7.443(3)]. Pd(bpy)Cl₂ forms long plates with stepped edges; the length of the crystal is parallel to *c* and the narrowest dimension is parallel to *b*. Pt(bpy)Cl₂ forms rectangular needles; the length of these crystals also is parallel to *c*, but the narrowest dimension is parallel to *a*. Thus, the orientation of the crystals could be determined from the morphology. Since these crystals are orthorhombic, the unit-cell axes are parallel to the crystal optical axes. The absorption experiments were carried out perpendicular to the [010] face for Pd(bpy)Cl₂ and perpendicular to the [100] face for Pt(bpy)Cl₂.

E. Synthesis

The preparations of several compounds whose properties are not discussed in detail in this chapter also are included in this section.

1. General Synthesis of $Pt(bpy)X_2$ Complexes

$Pt(bpy)Cl_2$ and $Pt(dmbpy)Cl_2$ were prepared as described by Morgan and Burstall³⁹ and later by Bielli and co-workers.⁴⁰ In a typical reaction, 2 g of $K_2[PtCl_4]$ in 150 ml H_2O was refluxed for 5 hours with 0.76 g bpy dissolved in 40 ml of 1 M HCl . The resulting bright yellow solid was isolated and washed with water, acetone and ether, before drying in a vacuum oven (95.3% yield). Yellow needles of $Pt(bpy)Cl_2$ are readily prepared by recrystallization from hot dmf (*N,N*-dimethylformamide).

A sample of $Pt(bpy)I_2$ was generously provided by Dr. V. M. Miskowski (Caltech). This material and $Pt(dmbpy)I_2$ were prepared by the method of Wimmer and co-workers.⁴¹ Crystals of $Pt(bpy)I_2$ suitable for X-ray diffraction studies were grown by slow evaporation from dmf .

The following method has proven superior for preparing $Pt(diimine)X_2$ complexes, including $Pt(bpy)Br_2$, $Pt(bpy)(CN)_2$, $Pt(bpy)(NCS)_2$, $Pt(dmbpy)(NCS)_2$, $Pt(phen)(NCS)_2$, $Pt(bpy)(NCO)_2$, $Pt(dmbpy)(NCS)_2$, $Pt(bpy)(N_3)_2$, $Pt(bpy)(NCS)_2$, $Pt(bpy)(oxalate)$, $Pt(bpy)(malonate)$, $Pt(bpy)(1,2-benzenedithiolate)$, $Pt(bpy)(catecholate)$, $Pt(bpy)(tert\text{-}butyl\text{-}catecholate)$, $Pt(bpy)(thiosalicylate)$, $Pt(bpy)(2\text{-}mercaptopyridinate)_2$, $Pt(bpm)(NCO)_2$, and $Pt(bpm)(CN)_2$. In a typical reaction, $Pt(bpy)Cl_2$ (0.2376 g) was dissolved in warm dmf or $dmso$ (dimethylsulfoxide) (~10 ml). The flask was wrapped in aluminum foil to minimize exposure to light. A slightly less than stoichiometric amount (99%) of solid $AgNO_3$ (0.1909 g) was added to the solution and the mixture was heated for 0.5 hour before allowing it to cool to room temperature without stirring. The $AgCl$ was efficiently removed by filtering the solution through a medium porosity frit with Celite; on occasion, a second filtration using another frit was necessary. At this point, an excess or slight excess of an appropriate nucleophile is added dropwise (usually in 1 ml dmf or H_2O) to the solution. In the case of $Pt(bpy)Br_2$, yellow microcrystals with an orange emission were obtained by recrystallization from dmf . Analysis (calc): C 23.53 (23.50); H, 1.30 (1.58); N 5.50 (5.48).

In several instances, the previous protocol was not successful; though these difficulties are mostly likely intrinsic to the synthetic targets. For example, an attempt to prepare $\text{Pt}(\text{bpy})(\text{SeCN})_2$ resulted in formation of a platinum mirror. Also, $\text{Pt}(\text{bpy})\text{F}_2$ is apparently too water sensitive to be synthesized in this manner. Efforts to prepare salts of $\text{Pt}(\text{bpy})(\text{diphenylphosphino-ferrocene})^{2+}$ gave an unstable, oily orange material. Listed below are the properties of several compounds prepared by the previous protocol, though these compounds are not discussed further in this chapter.

$\text{Pt}(\text{bpy})(\text{malonate})$ forms yellow needles with orange emission. Analysis (calc): C, 23.53 (23.50); H, 1.30 (1.58); N, 5.50 (5.48).

$\text{Pt}(\text{bpy})(\text{oxalate})$ forms a yellow solid with bright orange emission. The material appeared to be photosensitive, turning a gray color over time. Analysis (calc): C, 31.45 (32.81); H, 1.85 (2.84); N, 6.47 (6.38).

$[\text{Pt}(\text{bpy})(\text{Fcen})]^{2+}$ ($\text{Fcen}=1,6\text{-diferrocenyl-2,5-diazaheptane}$)⁴² forms red solids. X-ray diffraction data were collected for a crystal of the nitrate salt grown from water; however, though the Pt and one ferrocene moiety could be located, the structure could not be solved.

$\text{Pt}(5\text{-Cl-phen})(\text{CN})_2$ ⁴³ forms sparingly soluble orange and deep violet solids. We also observed a red form which may be a mixture of the orange and violet forms or a third isomer. One of these observed products may be the $[\text{Pt}(5\text{-Cl-phen})_2][\text{Pt}(\text{CN})_4]$ double salt. Since at least one of these products has a very intense red emission, further investigation is warranted.

2. $\text{Pt}(\text{dmpzH})_2(\text{dmpz})_2$

$\text{Pt}(\text{dmpzH})_2(\text{dmpz})_2$ ($\text{dmpzH}=3,5\text{-dimethylpyrazole}$) was synthesized according to the literature preparation for $\text{Pt}(\text{pzH})_2(\text{pz})_2$ ($\text{pzH}=\text{pyrazole}$).⁴⁴⁻⁴⁶ Initially, $\text{Pt}(\text{DMSO})_2\text{Cl}_2\cdot\text{H}_2\text{O}$ was prepared from $\text{K}_2[\text{PtCl}_4]$ as previously described.⁴⁶ Subsequent reaction with excess dmpzH in boiling water and precipitation with acetone

gave the colorless product in 84% yield. $\text{Pt}(\text{Me}_2\text{pzH})_4\text{Cl}_2\cdot\text{H}_2\text{O}$ was characterized by elemental analysis (calc): C 36.16% (35.93), H 4.80 (5.13), N 17.01 (16.76). Treatment of this complex in acetone with 6 N NaOH gave $\text{Pt}(\text{dmpzH})_2(\text{dmpz})_2$. The colorless product was characterized by ^1H NMR in CDCl_3 (δ , 1.71 and 1.61 ppm (12H); δ 5.43 ppm (2H); δ 18.37 ppm (1H)) and elemental analysis (calc): C 41.25% (41.59), H 5.15 (5.23), N 19.49 (19.40).

3. Potassium Pyrazolates

Potassium pyrazolates of pzH, dmpzH, and 3,4,5-trimethylpyrazole (tmpzH) were obtained by the same method described above. In a typical reaction, ~3 g potassium metal was added slowly to a solution of 7 g dmpzH in thf. After refluxing for 5 hours, a white hygroscopic solid was isolated. No analytical data were obtained. This reaction could not be extended to azaindole.

4. $\text{Pt}(\text{bpy})(\text{pz})_2$ and Related Compounds

$\text{Pt}(\text{bpy})(\text{pz})_2$ and its derivatives were synthesized using a modification of the literature preparation.⁴⁷ For example, 0.80 g $\text{K}(\text{dmpz})$ and 0.95 g of $\text{Pt}(\text{dmbpy})\text{Cl}_2$ were refluxed in approximately 20 ml. thf for 5 hours under argon. The filtered yellow solid was washed with ether. The raw product was more brightly colored if the starting platinum complex was recrystallized from dmf. The most successful methods of purification involved recrystallization from CH_2Cl_2 and then methanol. Crystals of $\text{Pt}(\text{dmbpy})(\text{dmpz})_2$ suitable for X-ray diffraction studies were grown by vapor diffusion of thf into a methanol solution of the complex.

The solvent of crystallization affects the color of these samples. For example, in the case of $\text{Pt}(\text{dmbpy})(\text{dmpz})_2$, wet samples are yellow, whereas dry samples are orange. Both forms exhibit orange emission at room temperature. These samples are identical in methanol and dichloromethane solution by ^1H NMR and UV-visible spectroscopy. The mass spectra are consistent with the chemical composition of the complexes. Both of the

tmpz derivatives are photochemically unstable in solution; and heating of $\text{Pt}(\text{bpy})(\text{dmpz})_2$ at 100° C over 24 hours in air resulted in decomposition.

Analysis⁴⁸ of the solid products indicates a tendency to retain a water of crystallization (Table 2.1). Samples that were dried under mild conditions (24 hours at 40° C under vacuum) contain 0.5 to 4 water molecules for every platinum complex. Some samples that were rigorously dried for days under vacuum at >80° C were 0.8% low in carbon and 0.4% low in nitrogen; oxygen was less than 1.3 % corresponding to fewer than 0.5 water molecules per platinum complex. Loss of water of crystallization was monitored by weight. With the exception of $\text{Pt}(\text{dmbpy})(\text{tmpz})_2 \cdot (\text{H}_2\text{O})$, solid samples used in spectroscopic studies contained 0.5 or fewer water molecules per platinum complex. These compounds are generally discussed without mention of water, though we are fully aware of the possible presence of solvent in these solids. The formation of a surface hydrate also is a consideration since these compounds were handled in an open atmosphere.

Table 2.2. Elemental analysis data for platinum(II) bipyridyl *bis*-pyrazolate complexes; calculated percentages shown in parentheses.

Compound	%C	%H	%N	%O
$\text{Pt}(\text{bpy})(\text{pz})_2 \cdot (\text{H}_2\text{O})$	38.27 (38.17)	2.94 (3.20)	16.84 (16.69)	1.58 (3.18)
$\text{Pt}(\text{bpy})(\text{pz})_2 \cdot 0.5(\text{H}_2\text{O})$	38.68 (38.87)	2.99 (3.06)	17.25 (17.0)	1.25 (1.62)
$\text{Pt}(\text{dmbpy})(\text{pz})_2 \cdot 0.5(\text{H}_2\text{O})$	41.38 (41.38)	3.51 (3.67)	16.28 (16.08)	1.00 (1.53)
$\text{Pt}(\text{dmbpy})(\text{pz})_2$	41.69 (42.11)	3.48 (3.53)	16.02 (16.37)	0.53 (—)
$\text{Pt}(\text{bpy})(\text{dmpz})_2 \cdot 0.5(\text{H}_2\text{O})$	43.70 (43.63)	4.08 (4.21)	15.27 (15.27)	0.87 (1.45)
$\text{Pt}(\text{bpy})(\text{dmpz})_2$	43.62 (44.36)	3.86 (4.09)	15.27 (15.52)	<0.5 (—)
$\text{Pt}(\text{dmbpy})(\text{dmpz})_2 \cdot 1.5(\text{H}_2\text{O})$	43.96 (44.29)	4.86 (4.90)	14.31 (14.09)	4.09 (4.02)
$\text{Pt}(\text{dmbpy})(\text{dmpz})_2 \cdot (\text{H}_2\text{O}) \cdot 0.4(\text{thf})$	45.52 (45.86)	4.94 (5.09)	13.52 (13.60)	—
$\text{Pt}(\text{dmbpy})(\text{dmpz})_2 \cdot 0.5(\text{H}_2\text{O})$	45.39 (45.67)	4.33 (4.70)	14.34 (14.52)	0.61 (1.38)
$\text{Pt}(\text{bpy})(\text{tmpz})_2 \cdot 0.5(\text{H}_2\text{O})$	45.26 (45.67)	4.65 (4.70)	14.46 (14.52)	1.20 (1.38)
(after rigorous drying)	45.45 (45.67)	4.53 (4.70)	14.61 (14.52)	1.20 (1.36)
$\text{Pt}(\text{dmbpy})(\text{tmpz})_2 \cdot (\text{H}_2\text{O})$	46.12 (46.82)	4.78 (5.24)	13.43 (13.65)	2.25 (2.60)

5. Preparation of $Pt(bpy)(pz)Cl$

This material was prepared under the same conditions as in the previous sections except using a 1:1 ratio of pyrazole to $Pt(bpy)Cl_2$. The isolated solid is yellow and exhibits no emission at room temperature. However, during recrystallization from CH_2Cl_2 , formation of the red form of this product was observed on several occasions. Emission from this product is intensely red at room temperature and is reminiscent of the red linear-chain form of $Pt(bpy)Cl_2$. The red and yellow solids appear interconvertible, and both give yellow solutions in DMSO and CH_2Cl_2 . Inducing formation of the red product has proven difficult and not wholly reproducible. For example, in one case, rotovapping a CH_2Cl_2 solution to dryness resulted in mostly red product. Repeating this process with the same re-dissolved sample sometimes yielded some red solid with mostly yellow material, and other times only yellow solid. Slow diffusion recrystallization of the yellow product from MeOH/Et₂O gave yellow needles (>99% of sample) and two small red crystals.

6. $Pt(dmbpy)^{2+}$ and $Pt(bpy)^{2+}$ in Aqueous Solution

The aqueous solution chemistry of platinum(II) 4,4'-dimethyl-2,2'-bipyridine is similar to that observed for 2,2'-bipyridine.⁴¹ The following products were observed: $Pt(dmbpy)(NO_3)_2$ [yellow] (pH<3), $(dmbpy)Pt(\mu-OH)_2Pt(dmbpy)^{2+}$ [orange] (3<pH<7), $(dmbpy)Pt(OH)_3Pt(dmbpy)^+$ [deep red] (7<pH<9), $Pt(dmbpy)(NO_3)_2$ [orange] (9<pH). Several of these complexes are intensely luminescent and likely candidates for the emissive impurities in $Pt(diimine)X_2$ compounds. For example, $[(bpy)Pt(\mu-OH)_2Pt(bpy)](NO_3)_2 \cdot H_2O$ exhibits an intense orange emission at room temperature (λ_{max} , 617 nm, fwhm 3200 cm⁻¹, τ 115 ns; 10 K: 637 nm, fwhm 3000 cm⁻¹; 77 K: τ 515 ns); analysis (calc): C, 27.44 (27.34); H, 2.19 (2.29); N, 9.10 (9.57).

E. X-ray Crystallography

Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer (MoK_α radiation and graphite monochromator). Intensities were corrected for Lorentz and polarization effects, as well as absorption (Ψ scans of six reflections). The intensities of three standard reflections showed no variations greater than those predicted by counting statistics. The Pt coordinates were obtained from Patterson maps, and remaining non-hydrogen atom positions were determined from successive structure-factor, Fourier calculations. Ligand H atoms were positioned by calculation (C-H, 0.95 Å) and were assigned isotropic B values approximately 1.1 times those of the attached carbon atoms. Weights were taken as $1/\sigma^2(F_o^2)$; variances $[\sigma^2(F_o^2)]$ were derived from counting statistics plus an additional term, $(0.014F_o^2)^2$. Variances of the merged data were determined by propagation of e.s.d.s plus another additional term, $(0.014\langle F_o^2 \rangle)^2$. Atomic scattering factors were taken from Cromer and Waber.^{49,50} Computer programs used were those of the CRYM crystallographic computing system⁵¹ and ORTEP.⁵² Pertinent data are collected in Table 2.3. Full details may be obtained from the Caltech X-ray Crystallography Facility.

III. Results and Discussion

A. Crystal Structures

In several instances, compounds were structurally characterized in order to identify intermolecular interactions which might significantly impact the electronic structure (see Chapters 3 and 4). For example, $\text{Pt}(\text{bpy})\text{Cl}_2$ exhibits dimorphism, crystallizing in a yellow form as discrete monomer units^{38,53} and in a red form as a linear chain with a Pt...Pt separation of 3.45 Å.^{54,55} We have noticed that the spectroscopic properties of the yellow bis(bromo) analogue strongly suggest that the complex exists in a monomeric environment in the solid state. However, the interpretation of the spectroscopy of the orange bis(iodo) species is less conclusive. It is uncertain whether

the orange color of crystalline $\text{Pt}(\text{bpy})\text{I}_2$ arises from a $\text{d}\sigma^* \rightarrow \pi^*(\text{bpy})$ charge-transfer transition associated with a dimer/linear-chain structure or a unimolecular $\text{d} \rightarrow \pi^*(\text{bpy})$ charge transfer red-shifted in the relatively weak N_2I_2 ligand field. Our determination of the structure of $\text{Pt}(\text{bpy})\text{I}_2$ establishes that the latter interpretation is preferred. Similarly, the crystal structure of $\text{Pt}(\text{dmbpy})(\text{dmpz})_2 \cdot (\text{H}_2\text{O}) \cdot 0.5(\text{thf})$ confirms that there are no short contacts between Pt atoms in this material. Thus, the observed luminescence from this compound originates from a unimolecular $^3\text{MLCT}$ state.

1. $\text{Pt}(\text{bpy})\text{I}_2$

The molecule, including the numbering system, is drawn in Figure 2.2a and the packing is shown in Figure 2.2b; selected distances and angles are given in Table 2.4. The molecule lies on a two-fold axis through the Pt atom. Distances and angles in the bipyridyl ligand are normal. The Pt-N bond to the bipyridyl (2.029(7) Å) and the N-Pt-N angle (79.3(3)°) are in close agreement with the values observed for the red form of $\text{Pt}(\text{bpy})\text{Cl}_2$ (2.009(6) Å and 80.2(2)°).^{54,55}

The Pt-I distance (2.589(2) Å) is consistent with observed bond lengths in other *cis*-bis(iodo)bis(N-donor) complexes. However, the intramolecular I··I separation (3.587(1) Å) and the corresponding I-Pt-I angle (87.71(3)°) are significantly smaller than those found in *cis*- $\text{Pt}(\text{NH}_3)_2\text{I}_2$ (3.765(1) Å and 93.40(4)°),⁵⁶ *cis*- $\text{Pt}(\text{C}_3\text{H}_5\text{NH}_2)_2\text{I}_2$ (3.780(2) Å and 94.26(4)°)⁵⁷ and $\text{Pt}(1,2\text{-benzoquinone dioxime})\text{I}_2$ (3.71 Å and 91.5(1)°).⁵⁸ This is a probable consequence of steric interactions involving the coplanar bipyridyl ligand and iodine atoms. Both the I··I intramolecular distance (3.587(1) Å) and the I··H1 intramolecular distance (2.825(1) Å) based on the calculated hydrogen positions are significantly shorter than the van der Waals distances.

The parallel monomer units stack to form a chain structure with consecutive molecules rotated by 180° (Figure 2.2c). Viewed on projection down *b*, the chain of

Table 2.3. Crystallographic data for Pt(bpy)I₂ and Pt(dmbpy)(dmpz)₂·(H₂O)·0.5(thf).

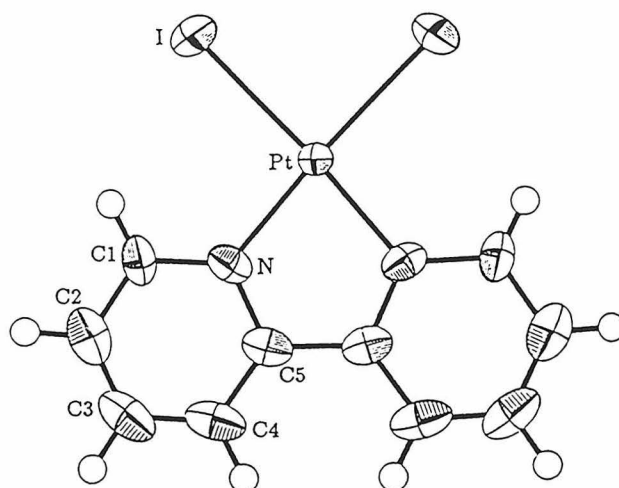
	Pt(bpy)I ₂	Pt(dmbpy)(dmpz) ₂ ·(H ₂ O)·0.5(thf)
formula	Pt(C ₁₀ H ₈ N ₂)I ₂	Pt(C ₅ H ₇ N ₂) ₂ (C ₁₂ H ₁₂ N ₂)] ·0.5(C ₄ H ₈ O)·H ₂ O
M_w	605.08	623.65
color	orange	yellow
crystal system	monoclinic	monoclinic
space group	<i>C2/c</i> (no. 15)	<i>P2₁/n</i> (no. 14)
a , Å	17.400(4)	8.625(2)
b , Å	9.809(2)	20.593(8)
c , Å	7.693(2)	14.451(4)
β , °	111.97(2)	90.32(2)
V , Å ³	1217.7(5)	2566.7(14)
D_{calc} , g/cm ³	3.30	1.61
Z	4	4
μ , cm ⁻¹	166.35	55.50
no. reflns	1070	4501
no. reflns $F_o^2 > 0$	1049	3933
no. reflns $F_o^2 > 3\sigma(F_o^2)$	956	1232
no. parameters	71	271
GOF ^a	2.24	1.49
R^b	0.032	0.062
$R(F_o^2 > 3\sigma(F_o^2))^b$	0.0268	0.039

^a $\text{GOF} = \left(\sum w(F_o^2 - F_c^2)^2 / (n - p) \right)^{1/2}$ where n is the number of data and p is the number of parameters refined.

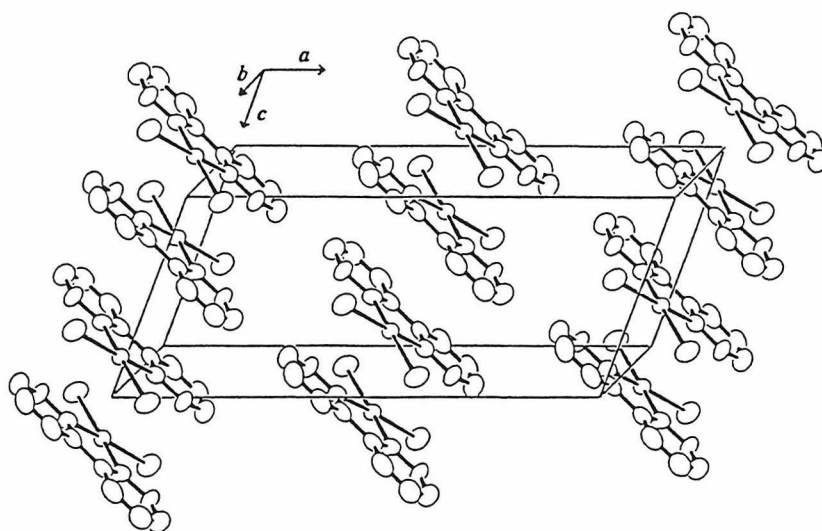
^b $R = \sum |F_o - |F_c|| / \sum |F_o|$

Figure 2.2 (a) An *ORTEP*⁵² drawing of the Pt(bpy)I₂ molecule with 50% probability ellipsoids showing the atomic numbering system. H atoms are shown as circles of arbitrary size. (b) A drawing of 12 molecules with one unit cell outlined (*Z*=4). The projection is roughly perpendicular to the *ac* plane, with the *a* axis horizontal; H atoms are not shown. (c) A drawing of two stacked molecules in the chain. The projection is perpendicular to the planes of the molecules.

(a)



(b)



(c)

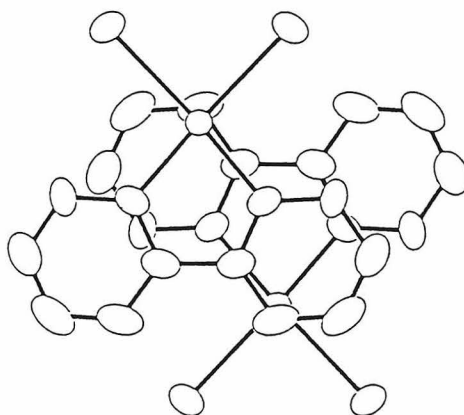
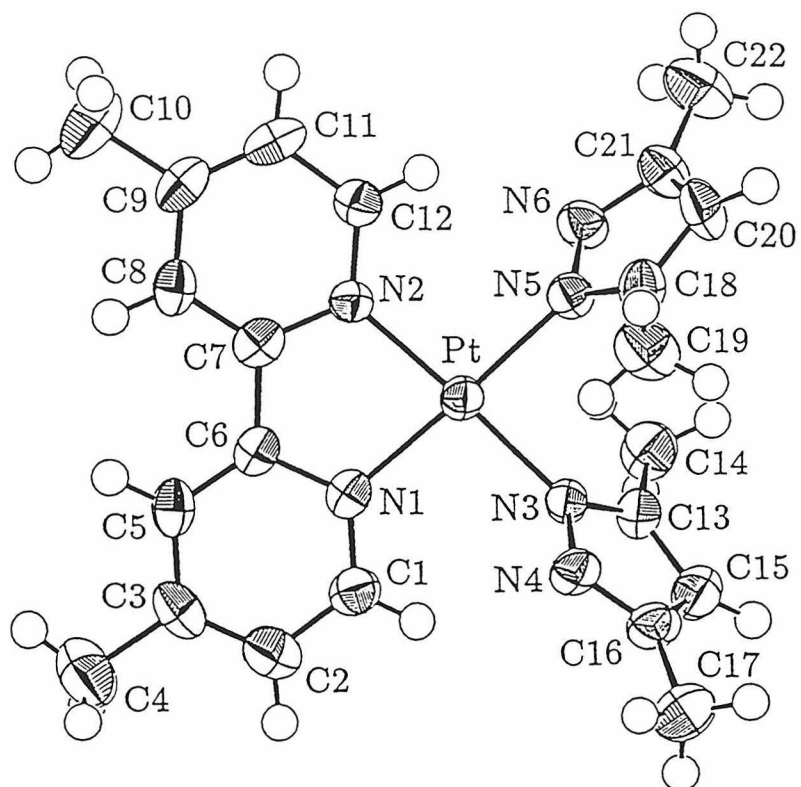
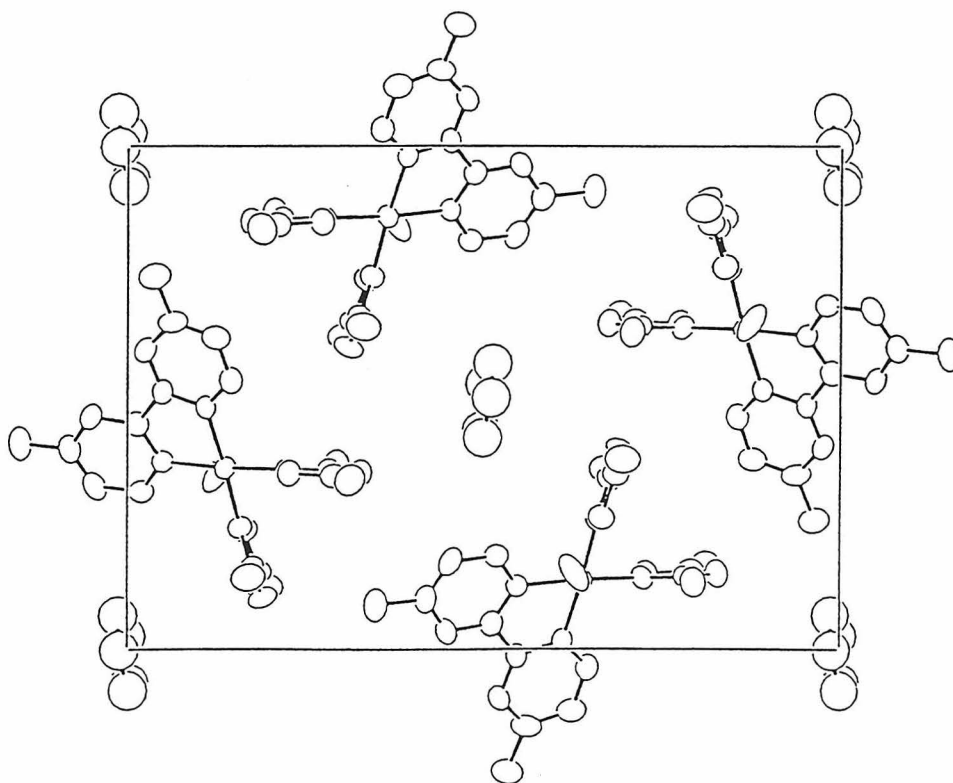


Figure 2.3 (a) An *ORTEP* drawing of the $\text{Pt}(\text{dmbpy})(\text{dmpz})_2$ molecule with 50% probability ellipsoids showing the atomic numbering system. H atoms are shown as circles of arbitrary size. (b) A projection view down the a axis showing the contents of one unit cell, plus three additional thf molecules. Only one molecular orientation is shown at each thf site.

(a)



(b)



molecules is parallel to the *c* axis and makes a nonzero angle (23.9°) with the normal to the molecular planes. Projection down the *a* axis reveals the zigzag structure of the chain resulting from the displacement of the platinum atoms by 3.63 Å along *b*. The view perpendicular to the planes of two consecutive molecules in a chain (Figure 2.2c) emphasizes their relative displacement. Thus, in contrast to the linear-chain structure of the red form of Pt(bpy)Cl₂ with nearly equal interplanar (3.402(1) Å) and Pt··Pt distances (3.449(1) Å),⁵⁵ the Pt··Pt separation (5.291(1) Å) in Pt(bpy)I₂ is considerably longer than the interplanar spacing (3.52 Å). The C3··C3 (3.445(17) Å) and Pt··C4 (3.510(11) Å) distances are the shortest intermolecular contacts. Evidently, significant metal-metal interaction (<3.5 Å) is precluded by the steric bulk of the iodine atoms.

2. *Pt(dmbpy)(dmpz)₂·(H₂O)·0.5(thf)*

A drawing of the molecule including the numbering system is shown in Figure 2.3a, and the packing is shown in Figure 2.3b. Selected distances and angles are given in Table 2.4. (The thf molecule is located near a center of symmetry and its parameters could not be refined; therefore, an idealized thf molecule was positioned based on difference maps.) The Pt-N distances to the bipyridyl N atoms are equal at 2.009(13), and to the pyrazolyl N atoms at 1.983(11) Å. Distances and angles in the ligand atoms are normal, with C-CH₃ bonds being a little short, especially in the pyrazolyl ligands (C18-C19 = 1.449(14) Å is the shortest). Each pyrazolyl ligand is twisted out of the Pt-bipyridyl plane by 64(3)°. This orientation is comparable to other *cis*-bis(nitrogen heterocycle) platinum(II) systems: 41.7° for *cis*-[Pt(*N*-methylimidazole)₂Cl₂],⁵⁹ and 55.3° and 73.2° for *cis*-[Pt(pyrazole)₂Cl₂].⁶⁰

The water molecule is 2.82(1) Å from N4 of one complex and 2.84(1) from N6 of an adjacent complex; the resulting N4··O··N6 angle is 108(1)°. Thus, the molecules pack to form a chain of complexes connected by hydrogen bonds from the pyrazolate non-coordinating nitrogen to a bridging water. We surmise from this structure that the

tendency for the pyrazolyl complexes to tenaciously retain water of crystallization can be attributed to the basicity of the pyrazolate ligands. There are short distances between N3 and C19 (3.32(1) Å) and N5 and C14 (3.33(1) Å). The H atoms on C14 and C19 show up as two sets of three H atoms each in the plane where they are expected, but none of them points toward the close N atom. There are longer contacts between the water molecule and C5 and C8 in an adjacent molecule (3.30(1) and 3.20(1) Å). The Pt...O(water) distance (4.492 (7) Å) and all other distances are at van der Waals distances or greater.

Table 2.4. Selected bond lengths (Å) and angles (°) for Pt(bpy)I₂ and Pt(dmbpy)(dmpz)₂·(H₂O)·0.5(thf).^a

Pt(bpy)I ₂			
Pt-I	2.006 (8)	N-Pt-I	96.5 (2)
Pt-N	2.294 (3)	N-Pt-I'	175.8 (2)
N-C1	1.339 (12)	N-Pt-N'	79.3 (3)
C5-C5'	1.463 (13)	I-Pt-I'	87.7 (1)
Pt(dmbpy)(dmpz) ₂ ·(H ₂ O)·0.5(thf)			
Pt-N1	2.018 (7)	N1-Pt-N2	80.4 (3)
Pt-N2	2.000 (7)	N1-Pt-N3	94.8 (3)
Pt-N3	1.975 (7)	N1-Pt-N5	176.2 (3)
Pt-N5	1.990 (7)	N2-Pt-N3	175.2 (3)
N1-C6	1.376 (11)	N2-Pt-N5	95.8 (3)
N2-C7	1.363 (11)	N3-Pt-N5	89.0 (3)

^a Primed atoms are related by a twofold axis: -x, y, 1/2-z.

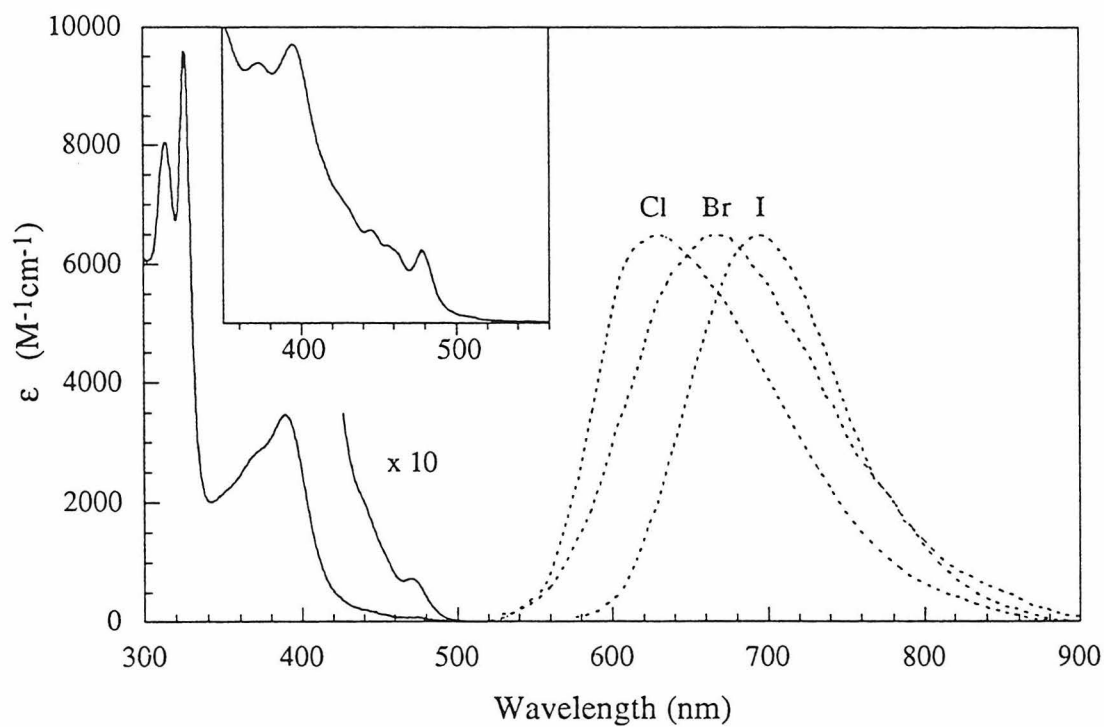
B. Absorption Spectroscopy of $\text{Pt}(\text{bpy})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) Complexes

The absorption spectrum of $\text{Pt}(\text{bpy})\text{Cl}_2$ in dmf (Figure 2.4) is characteristic of many platinum(II) bipyridyl complexes. As noted by Gidney, Gillard and Heaton,²⁴ the intense vibronic structure at 315 and 326 nm ($\Delta\nu \sim 1100 \text{ cm}^{-1}$) is only weakly dependent on solvent (H_2O : 307, 318; dichlorobenzene: 317, 329 nm), and this band arises from the lowest energy transition to the $^1\pi \rightarrow \pi^*$ state of bipyridine. Accordingly, this band is almost completely insensitive to the nature of the ancillary ligand. Indeed, similar vibronic structure is found in the spectra of the bromo and iodo derivatives in dmf (Figure 2.5 and Table 2.5). (In the spectrum of $\text{Pt}(\text{bpy})\text{I}_2$, a high-lying $^1\text{MLCT}$ band partially obscures this structure.) In fact, this band appears *more* sensitive to changes in solvent than to changes in the ancillary ligands. Thus, in dmf solution the progression shifts only modestly to lower energy ($\sim 150 \text{ cm}^{-1}$) when Cl is replaced by I. Similarly, in aqueous solution the first vibronic $^1\pi \rightarrow \pi^*$ features in the spectra of $\text{Pt}(\text{bpy})\text{Cl}_2$ and $\text{Pt}(\text{bpy})(\text{en})^{2+}$ are nearly coincident, maximizing at 318 and 316 nm, respectively. These small variations suggest that the ancillary ligands only weakly perturb the electronic structure of the bipyridyl ligand.

The lower energy feature maximizing at 393 nm (ϵ 2700), with shoulders at 377 and 356 nm, in Figure 2.4 is strongly solvent sensitive (H_2O : 345; dichlorobenzene: 411 nm) and has been assigned as a $^1\text{MLCT}[\text{d}\pi(\text{Pt}) \rightarrow \pi^*(\text{bpy})]$ transition.^{24,53} The shift of this band to lower energy in the spectra of the bromo (372, 395 nm) and iodo (388, 415sh nm) derivatives is consistent with the relative electronegativities²⁴ and ligand field strengths of these halides: $\text{Cl} > \text{Br} > \text{I}$. The same trend is evident in the diffuse reflectance spectra for this series (Figure 2.6), confirming the fact that this transition is strongly influenced by the nature of the ancillary ligands. Thus, this band is blue-shifted in the aqueous solution spectrum of $\text{Pt}(\text{bpy})(\text{en})^{2+}$ ($\sim 330 \text{ nm}$).¹¹ The relatively low energy of this absorption in the spectra of the halide derivatives is attributable to the strong π -donor properties of these ligands.²³

Figure 2.4 (a) Room temperature absorption spectrum of Pt(bpy)Cl₂ in dmf (solid line). Emission spectra of: Pt(bpy)Cl₂ in dilute butyronitrile solution at 77 K (adapted from the work of Miskowski and Houlding),¹¹ and microcrystalline samples of Pt(bpy)Br₂ and Pt(bpy)I₂ at 10 K. Inset shows diffuse reflectance data displayed as an absorption spectrum for Pt(bpy)Cl₂ at room temperature. (b) Plot of the ¹π→π*, ¹MLCT, and ³π→π* band maxima vs. the maxima of the lowest ¹MLCT band (left) and vs. Reichardt's solvent E_T-values.⁶¹ As reported previously for several spin-allowed transitions in the spectrum of Pt(bpy)Cl₂,²⁴ the maximum of these bands show a linear dependence on Reichardt's solvent E_T-values.⁶¹ Data shown are for absorption spectra measured in acetonitrile, propylene carbonate, dmf, 1-methyl-2-pyrrolidinone (nmp), methylene chloride, dichloroethane, and dichlorobenzene. The slopes are indicated by *s*; the energy ³π→π* transition shows a solvent dependence intermediate between that of the ¹π→π* and ¹MLCT transitions.

(a)



(b)

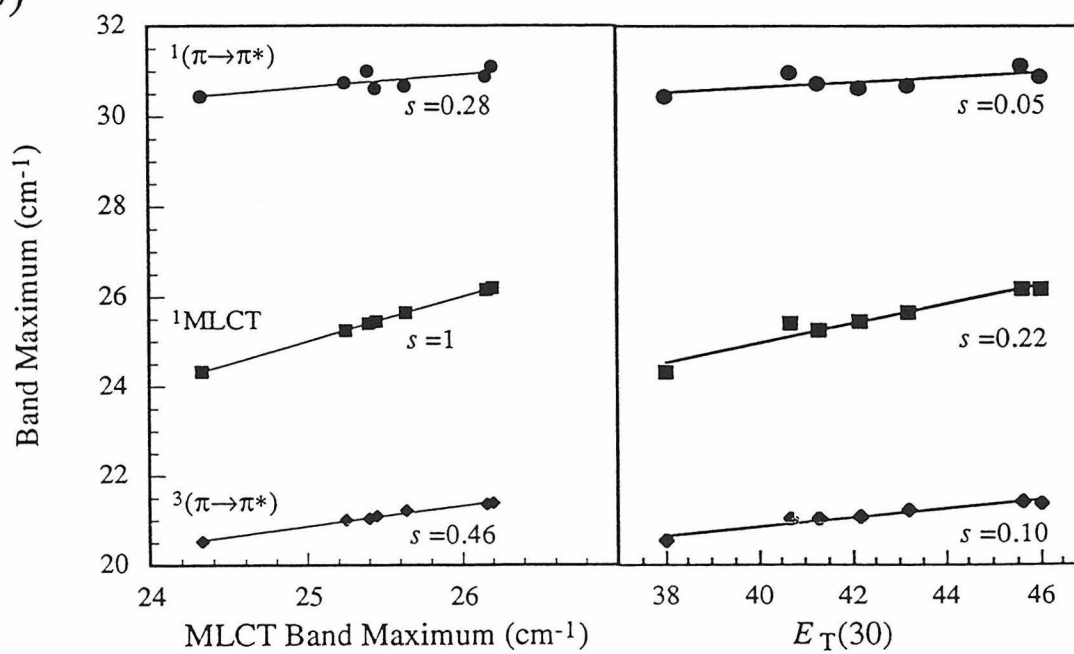
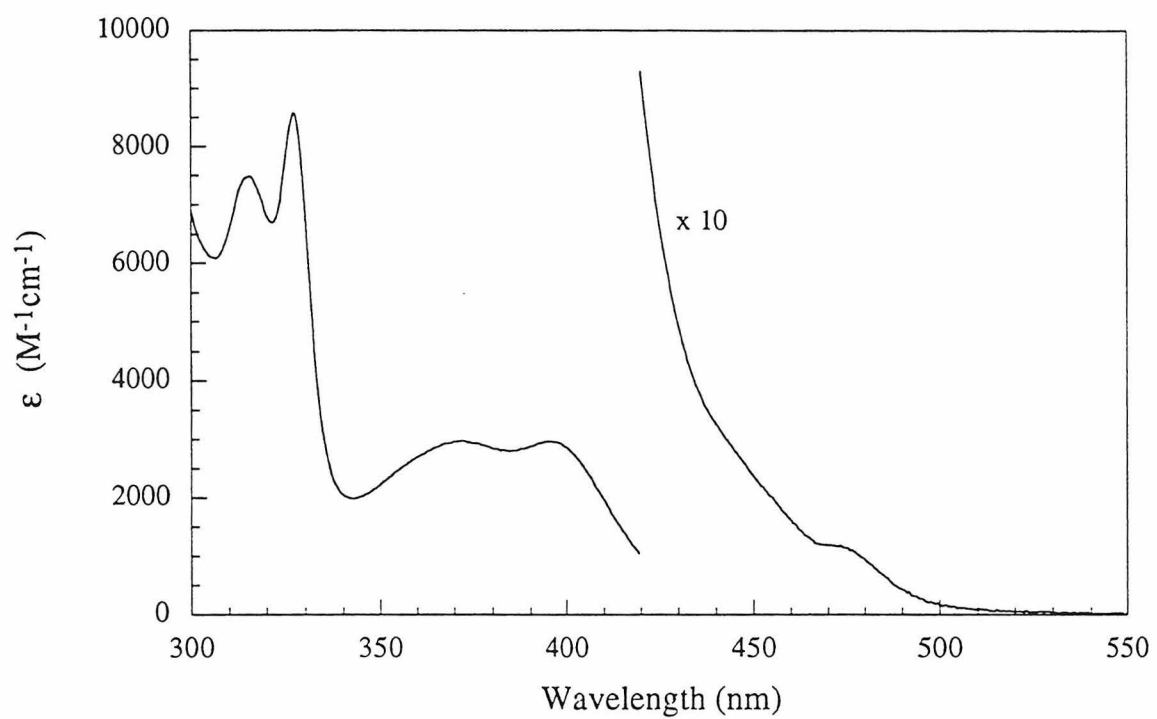


Figure 2.5 Room temperature absorption spectra of (a) $\text{Pt}(\text{bpy})\text{Br}_2$ and (b) $\text{Pt}(\text{bpy})\text{I}_2$ in dmf.

(a)



(b)

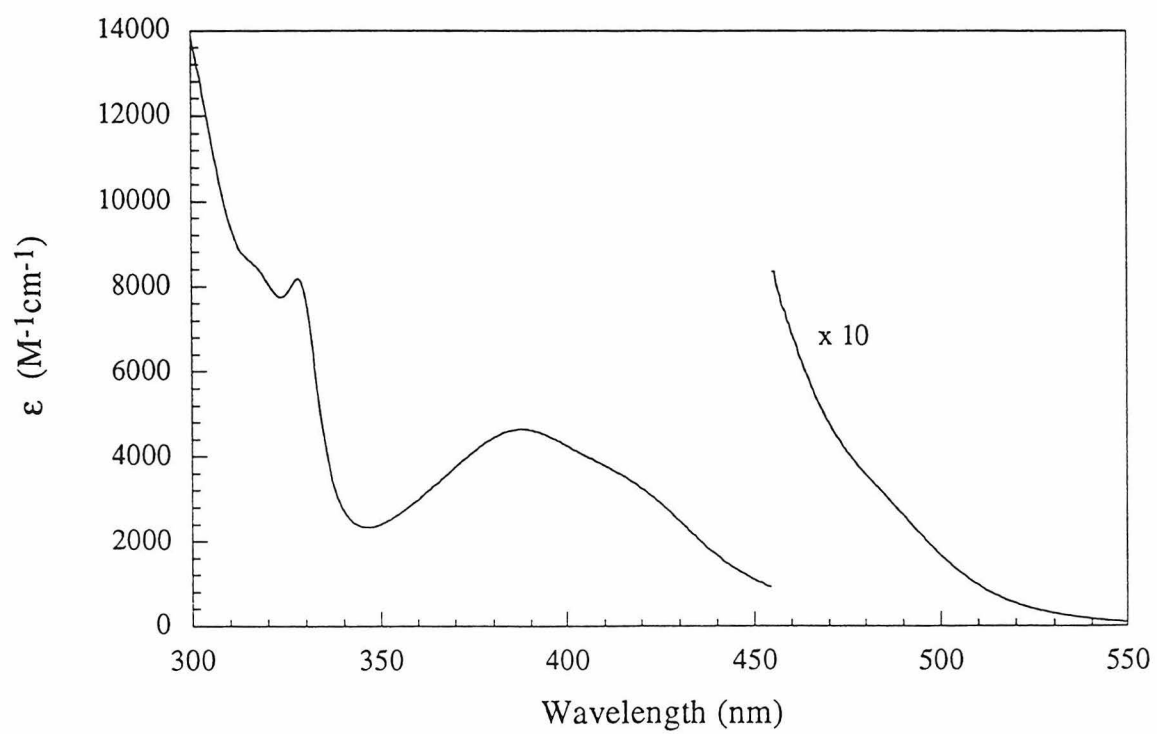


Figure 2.6 Diffuse reflectance data displayed as absorption spectra for $\text{Pt}(\text{bpy})\text{X}_2$ complexes ($\text{X}=\text{Cl}, \text{Br}, \text{I}$).

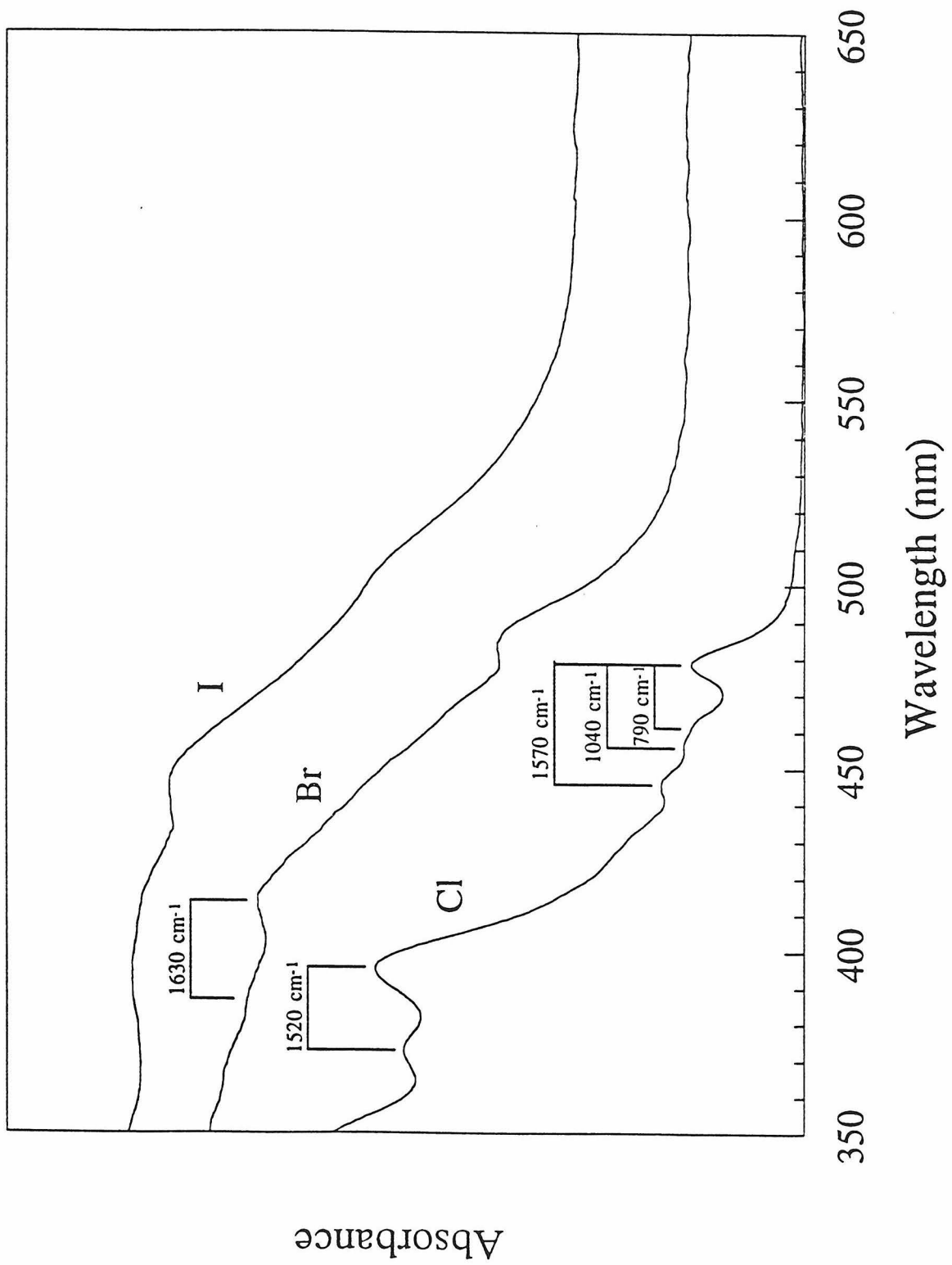


Table 2.5. Absorption spectral data for Pt(bpy)X₂ (X=Cl, Br, I) in dmf.

Transition	Pt(bpy)Cl ₂	Pt(bpy)Br ₂	Pt(bpy)I ₂
¹ π→π*, nm	314.5, 326	315.5, 327	316sh, 328
[ε, M ⁻¹ cm ⁻¹]	[8050, 9590]	[7500, 8580]	[8560, 8180]
(Δv, cm ⁻¹)	(1100)	(1100)	(1150)
¹ MLCT	357sh, 373sh, 390	372, 395	388, 415sh
[ε, M ⁻¹ cm ⁻¹]	[2350, 2880, 3470]	[2980, 2970]	[4640, 3540]
(Δv, cm ⁻¹)	(1200, 1150)	(1550)	(1700)
³ π→π*	471	475sh	483sh
[ε, M ⁻¹ cm ⁻¹]	[70]	[120]	[340]

Interestingly, the ¹MLCT[dπ→π*] band is structured, giving the appearance of at least two overlapping bands or a single vibronic progression. This structure is well-resolved in a glassy butyronitrile solution of Pt(bpy)Cl₂ at 77 K,¹¹ with spacings of ~1350 and ~1670 cm⁻¹. There are at least two possibilities for this pattern. We can rule out a transition involving a slightly higher energy bipyridyl π* level because the next highest π*(a₂) level lies ~7000 cm⁻¹ higher in energy than the lowest π*(b₁) level.⁶²⁻⁶⁵ The observed spacings in the spectra of the Pt(bpy)X₂ (X = Cl, Br, I) series are consistent with a vibronic progression in the MLCT absorption band associated with the bipyridyl ligand stretching modes (Table 2.5). Alternatively, since the dπ(xz,yz,x²-y²)→π* ¹MLCT components are expected to split in C_{2v} symmetry, the apparent splitting of the absorption band could reflect a splitting of the dπ levels. However, it is not obvious that this is the situation. As predicted by MO calculations, the d_{yz}→d_{xy} and d_{xz}→d_{xy} transitions in *cis*-PtN₂Cl₂ complexes (*e.g.*, Pt(en)Cl₂, Pt(NH₃)Cl₂, and Pt(pyridine)₂Cl₂) are not resolved in solution spectra; in contrast, the observed spacings between the spin-allowed d_{xz,yz}(b₁,a₂)→d_{xy} and d_{x²-y²}(a₁)→d_{xy} transitions (3700, 3000 and 5200 cm⁻¹, respectively) are somewhat larger than the splitting of Pt(bpy)X₂ MLCT band.

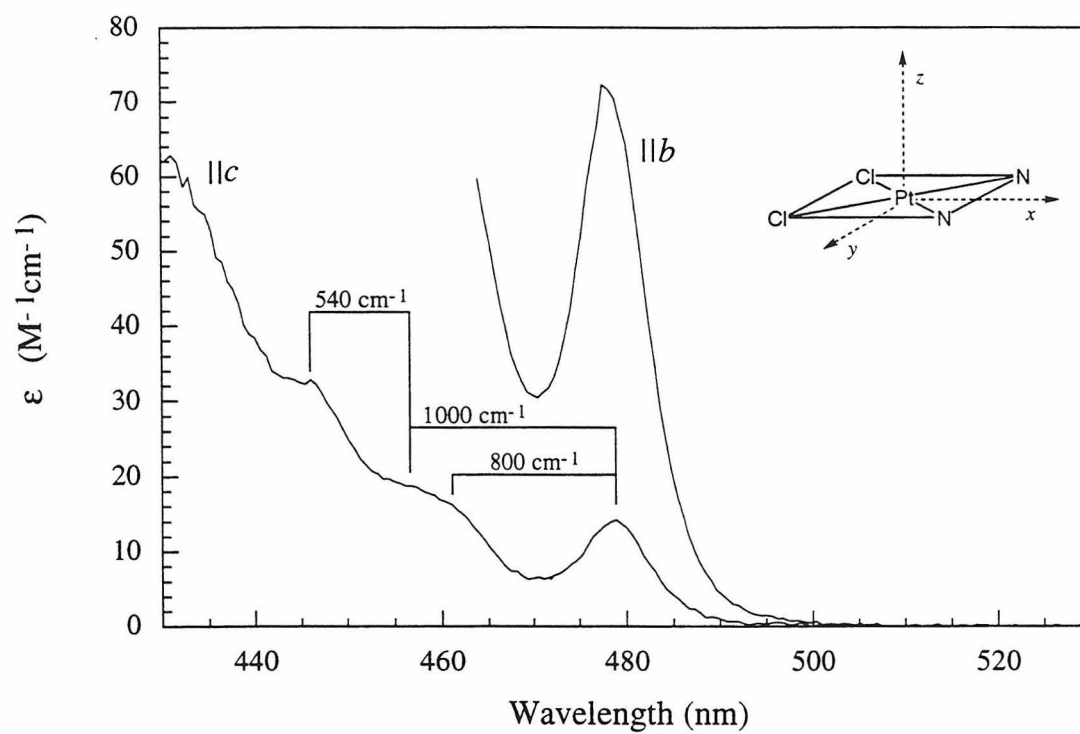
Moreover, from overlap considerations, the $d_{xz}(b_1) \rightarrow \pi^*$ transition is expected to carry considerably more oscillator strength than either the $d_{yz}(a_2) \rightarrow$ or $d_{x^2-y^2}(a_1) \rightarrow \pi^*$ transitions (x bissects the diimine ligand as in Figure 2.1). Despite these considerations, the possibility of two $^1\text{MLCT}$ absorption bands cannot be excluded since Kaim and co-workers⁶⁶ report evidence for at least two MLCT absorption bands in the spectra of $\text{Pt}(\text{diimine})(\text{alkyl})_2$ complexes - the electron donating groups in these complexes shift the manifold of MLCT features to lower energies where they are not obscured by $^1\pi \rightarrow \pi^*$ absorption.

The lowest energy feature in the solution absorption spectrum of $\text{Pt}(\text{bpy})\text{Cl}_2$ is particularly intriguing. This band is weak and moderately solvent sensitive occurring at 487 nm in dichlorobenzene, 474 nm (ϵ 80) in nmp, and 467 nm in acetonitrile. This feature also appears in the diffuse reflectance spectra of both the red (Chapter 4) and yellow forms (479 nm; Figure 2.4 and 2.7) of $\text{Pt}(\text{bpy})\text{Cl}_2$, as well as in the single-crystal polarized absorption spectrum of the red form.⁶⁷ Furthermore, we find a similar feature in the solution absorption spectra (Figure 2.5) and diffuse reflectance spectra (Figure 2.6) of the bromo (dmf: 475sh nm, ϵ 120) and iodo (dmf: 483sh nm, ϵ 340) derivatives. Thus, the energy of this transition is only modestly dependent on the ancillary ligands, shifting slightly to lower energy when Cl is replaced by Br ($\sim 200 \text{ cm}^{-1}$) or I ($\sim 500 \text{ cm}^{-1}$). For comparison, the $^1\text{MLCT}$ band shows a larger red-shift when Cl^- is replaced by Br ($\sim 300 \text{ cm}^{-1}$) or I ($\sim 1500 \text{ cm}^{-1}$).

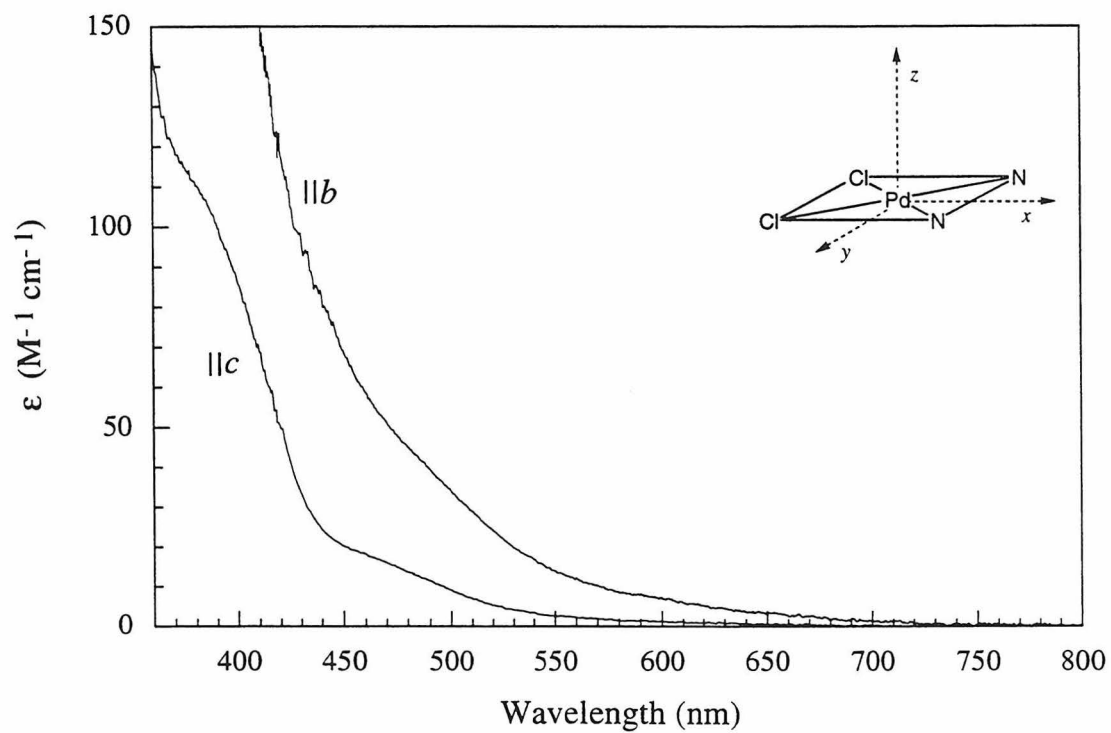
The energy and intensity of this band are consistent with a transition to a LF, $^3\pi \rightarrow \pi^*$ or $^3\text{MLCT}$ state. However, the weak dependence on ligand field strength argue against a MLCT or $d \rightarrow d$ (LF) transition. In fact, the well-resolved vibronic structure (Figure 2.7) is strikingly similar to that of the $^1\pi \rightarrow \pi^*$ progression at higher energy. Moreover, this vibronic structure shares a mirror-image relationship with $^3\pi \rightarrow \pi^*$ emission profiles observed for $\text{Pt}(\text{bpy})\text{X}_2$ complexes with strong-field ancillary ligands

Figure 2.7 Single-crystal polarized absorption spectra for (a) Pt(bpy)Cl₂ (yellow form) and (b) Pd(bpy)Cl₂. Pt(bpy)Cl₂ (*a* 18.257(4), *b* 15.795, *c* 7.443(3) Å) is isomorphous with Pd(bpy)Cl₂, crystallizing in *Pbca* (no. 61) with *Z*=8.³⁸ The nearly planar units stack along the *c* axis with consecutive molecules related by a *c*-glide plane. The complexes are only weakly interacting; both the interplanar spacings (*c*/2: Pt(bpy)Cl₂, 3.722(2); Pd(bpy)Cl₂, 3.747(1) Å) and metal...metal (Pd...Pd, 4.587(2); Pt...Pt, Å) contacts are relatively long. In the case of the Pt crystal, absorption spectra were recorded perpendicular to the [100] plane; for the Pd crystal, spectra were recorded perpendicular to the [010] plane. The spectra labelled *llc* were recorded with light polarized parallel to the stacking direction (*c* axis); this direction is nearly parallel to the molecular *z* axis. The spectra labelled *llb* were recorded with light polarized parallel to the *a* axis. The molecules are not well aligned in the latter direction. Using the available coordinates from the isomorphous Pd structure,³⁸ the PdN₂ unit defines the molecular axes, *x*, *y* and *z*. Then, the *I*(*llb*)/*I*(*llc*) intensity ratios for *x*-, *y*- and *z*-polarized transitions for Pt(bpy)Cl₂ are 15.7, 3.8 and 0.001, respectively. The observed value for *I*(*llb*)/*I*(*llc*) at 478 nm is 5.1, clearly most consistent with *x*-polarization. (*I*(*llb*)/*I*(*llc*) is 6.0 if the molecular axes are defined by the PdCl₂ unit.)

(a)



(b)



(see Figure 2.13 and Chapter 4). Therefore, we assign this feature to a spin-forbidden transition to a $^3\pi\rightarrow\pi^*$ state.

Several observations suggest that this transition has partial metal character. Most notably, the band is more intense and originates at slightly lower energy than observed for our $\text{Pt}(\text{bpy})(\text{en})^{2+}$ (447 nm, ϵ 4)¹¹ and $\text{Ir}(\text{bpy})_3^{3+}$ (450 nm, ϵ 10)¹⁰ model complexes. Additionally, this transition shows a weak solvent dependence that is intermediate to that of the $^3\pi\rightarrow\pi^*$ or $^3\text{MLCT}$ absorption bands (Figure 2.4). Therefore, we have considered two limiting spin-orbit coupling mechanisms that could introduce metal character, and therefore intensity, into this transition. The first is the intensity-stealing mechanism which involves mixing with a specific state; the extent of this interaction is inversely related to the energy gap between the two states.⁶⁸ Thus, a possible candidate for this type of mixing is the low-lying $^1\text{MLCT}[\text{d}\pi\rightarrow\pi^*]$ state. The second mechanism is the internal heavy-atom effect⁶⁹ which involves relaxation of the spin-selection rule by spin-orbit coupling; the triplet $\pi\rightarrow\pi^*$ transition effectively steals intensity from the corresponding singlet $\pi\rightarrow\pi^*$ transition. We emphasize that, in this case, the singlet-triplet transition retains the vibronic coupling characteristics of the pure $\pi\rightarrow\pi^*$ transition. Thus, this mechanism is entirely consistent with the diffuse reflectance and single-crystal absorption (*vide infra*) data which show well-resolved $\pi\rightarrow\pi^*$ vibronic structure.

In analogy to organic systems,⁶⁹ the diffuse bipyridyl π^* orbitals are expected to be dominant in the second mechanism, since overlap of the ligand orbitals with those of the platinum (with its large spin-orbit coupling constant) leads to relaxation of the spin selection rule. In fact, recently Hill and co-workers⁷⁰ have established, through analysis of EPR data, that the predominantly ligand-centered π^* LUMO of $\text{Pt}(\text{tpy})\text{Cl}^+$ (tpy = 2,2':6',2''-terpyridine) has 3-4% $p_z(\text{Pt})$ character. This results in a significant stabilization ($\sim 5000\text{ cm}^{-1}$) of this orbital with respect to the corresponding $\text{Zn}(\text{tpy})\text{Cl}_2$ complex. Interestingly, the tpy $^1\pi\rightarrow\pi^*$ transitions for the Pt complex are only modestly shifted (1500 cm^{-1}) to lower energy of the transitions for the Zn complex due to a nearly

compensating stabilization of the π level of the Pt complex *via* $d_{xz,yz}$ interaction. Studies^{66,71} of Pt(bpy) complexes indicate that similar mixing occurs for these compounds. Thus, in the case of Pt(bpy)Cl₂, we expect that strong π -electron donation by the Cl⁻ ligands tends to expand the metal orbitals, enhancing π^* - p_z (Pt) overlap. This effect accounts, at least in part, for the increased intensity and the slightly lower energy of the $^3\pi \rightarrow \pi^*$ transition with respect to Pt(bpy)(en)²⁺.

The single-crystal polarized absorption spectra indicate that this very narrow band is strongly allowed for light polarized parallel to the crystal *b* axis (*llb*) - that is, approximately in the plane of the molecule (478 nm, ϵ 72, fwhm 430 cm⁻¹). The transition is considerably weaker for light polarized parallel to *c* (ϵ 14); see Figure 2.7a. We note that the first vibronic feature of the spin-allowed $\pi \rightarrow \pi^*$ transition in solution also is characteristically narrow (326 nm, fwhm 650 cm⁻¹). From the isotropic extinction coefficient of approximately 70 M⁻¹cm⁻¹ and the available coordinates for the isomorphous Pd structure,³⁸ the crystal extinction coefficients (M⁻¹cm⁻¹) were predicted for three cases of dipole selection rules:

	<i>x</i> -polarized	<i>y</i> -polarized	<i>z</i> -polarized	observed
<i>lla</i>	52	132	26	not measured
<i>llb</i>	148	62	0.2	72
<i>llc</i>	9.5	16	184	14

The experimental data are in closest agreement with the a dipole-allowed transition with *y*-polarization; the other two possibilities agree very poorly. The spin-orbit components of the $^3B_2 \pi \rightarrow \pi^*$ state have A₁, A₂ and B₁ symmetry; thus, transitions to these states are formally *x*-polarized, forbidden and *z*-polarized, respectively. The fact that the $^3\pi \rightarrow \pi^*$ transition is observed to be strongly *y*-polarized is entirely consistent with our notion of strong coupling with the corresponding singlet transition which is, in fact, strongly *y*-polarized. Since there is already considerable mixing of the platinum $d\pi$ and p_z orbitals

with the ligand π and π^* orbitals, only a vibronic or static perturbation is necessary to allow coupling of the singlet and triplet transitions.

Table 2.6. Selection rules (in italics) for some electronic transitions of platinum(II) diimine complexes with spin-orbit coupling. Symmetry labels refer to double group C_{2v} . Coordinates are defined in Figure 2.1.

Transition	States of Singlet Parentage			States of Triplet Parentage	
$\pi(a_2) \rightarrow \pi^*(b_1)$	B_2 (1B_2)	<i>y</i>		A_1, A_2, B_1 (3B_2)	<i>x, -, z</i>
$d_{x^2-y^2}(a_1) \rightarrow \pi^*(b_1)$	B_1 (1B_1)	<i>z</i>		A_1, A_2, B_2 (3B_1)	<i>x, -, y</i>
$d_{yz}(a_2) \rightarrow \pi^*(b_1)$	B_2 (1B_2)	<i>y</i>		A_1, A_2, B_1 (3B_2)	<i>x, -, z</i>
$d_{xz}(b_1) \rightarrow \pi^*(b_1)$	A_1 (1A_1)	<i>x</i>		A_2, B_1, B_2 (3A_1)	<i>-, z, y</i>
$d_{z^2}(a_1) \rightarrow \pi^*(b_1)$	B_1 (1B_1)	<i>z</i>		A_1, A_2, B_2 (3B_1)	<i>x, -, y</i>

For comparison, the single crystal absorption spectrum of the palladium analogue, $\text{Pd}(\text{bpy})\text{Cl}_2$, is shown in Figure 2.7b. Again, there is a moderately in-plane polarized feature at ~ 470 nm (ϵ 50), as well as a more intense band near 370 nm. (There also may be one or more weaker bands at longer wavelengths, ~ 525 and 575 nm). However, in this case this broad weak band is characteristic of a spin-forbidden ligand field transition. In fact, these lowest energy features are qualitatively similar to the lowest energy $^3d \rightarrow d$ bands (of similar intensity) in the spectra of PdCl_4^{2-} and PtCl_4^{2-} . These latter transitions also are strongly *xy* polarized. (However, we note that there are distinct differences between the polarized absorption spectra of $\text{Pd}(\text{bpy})\text{Cl}_2$ and those of $\text{Pd}(\text{en})\text{Cl}_2$ and $\text{Pt}(\text{en})\text{Cl}_2$.)⁷² Thus, in the case of $\text{Pt}(\text{bpy})\text{Cl}_2$, the lowest ^3LF bands apparently lie buried under the 478 nm band; as expected, the lowest $d \rightarrow d$ bands are blue-shifted with respect to the palladium analogue.

There are three features near the 478 nm band in both the single-crystal and diffuse reflectance spectra (Figures 2.6 and 2.7a). The two higher energy features, shifted by ~ 1000 and 1500 cm^{-1} to the blue of the 478 nm band, are attributable to a vibronic progression associated with the characteristic $1000\text{--}1500\text{ cm}^{-1}$ vibrational modes

of the bipyridyl ligand. A similar feature is observed in the dmf solution absorption spectrum (440sh nm, ϵ 200). These spacings are comparable to those observed for the spin-allowed $\pi \rightarrow \pi^*$ transition (295 K nmp: $\sim 1100 \text{ cm}^{-1}$; 77 K butyronitrile glass: $\sim 1040 \text{ cm}^{-1}$). In aqueous solution, the $^3\pi \rightarrow \pi^*$ band of $\text{Pt}(\text{bpy})(\text{en})^{2+}$ exhibits two features separated by $\sim 1500 \text{ cm}^{-1}$. For $\text{Ir}(\text{bpy})_3^{2+}$, a 1300-1500 cm^{-1} progression is observed. In contrast, the feature at 461 nm is shifted by only 800 cm^{-1} from the 478 nm band, and thus, may mark the origin of another band, such as the lowest $^3\text{MLCT}$. Using an estimated singlet-triplet splitting of 3700 cm^{-1} (between the room temperature $^1\text{MLCT}$ absorption maximum and the $^3\text{MLCT}$ 0-0 energy),²³ we predict the $^3\text{MLCT}$ 0-0 energy to be at 463 nm in the solid state (based on the diffuse reflectance spectrum). However, it should be noted that in the 10 K single-crystal absorption spectrum of $\text{Pt}(\text{bpm})(\text{CN})_2 \cdot \text{H}_2\text{O}$ (bpm=2,2'-bipyrimidine), vibronic structure with spacings of 356, 763, 1002, and 1514 (± 30) cm^{-1} are observed.⁷³ Thus, the feature at 461 nm also could belong to the $^3\pi \rightarrow \pi^*$ vibronic progression.⁷⁴

C. Emission Spectroscopy of $\text{Pt}(\text{bpy})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) Complexes

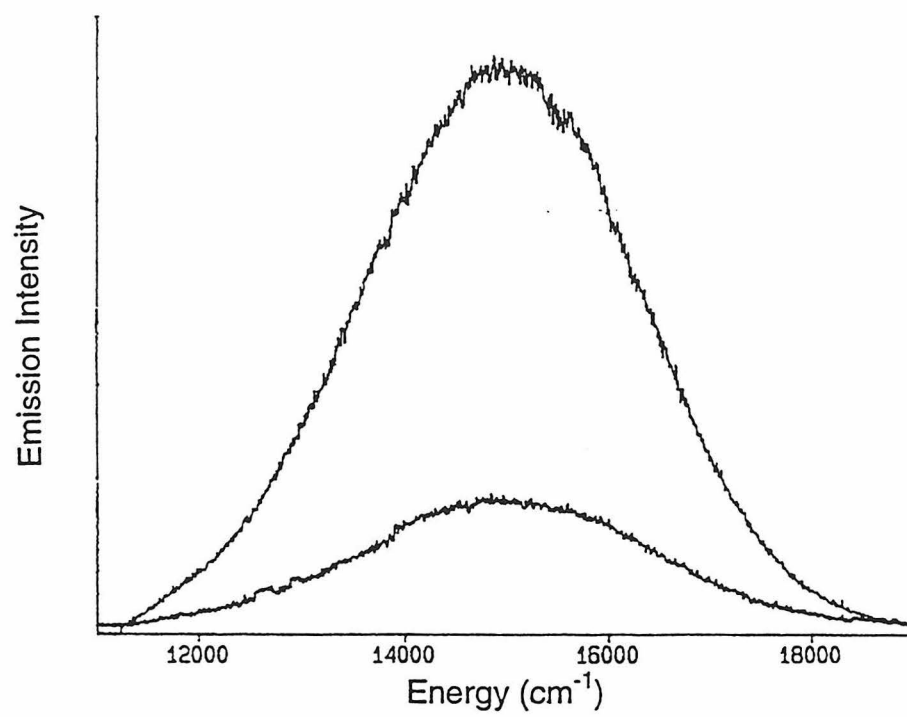
Luminescence spectra for these three compounds are shown in Figure 2.4. Room-temperature and low-temperature spectra are shown for the bromo and iodo derivatives in Figure 2.8, and photophysical properties are summarized in Table 2.7.

Table 2.7. Photophysical properties of microcrystalline $\text{Pt}(\text{bpy})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).^{2,23}

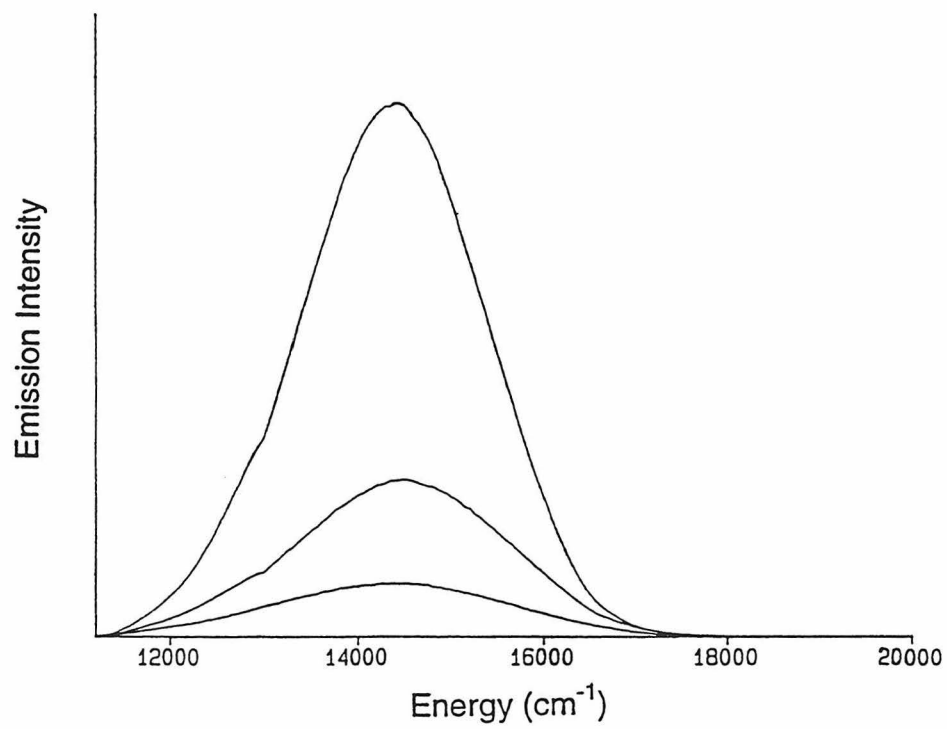
Compound	Room Temperature			10 K		
	λ_{max} (nm)	fwhm (cm^{-1})	τ (μs)	λ_{max} (nm)	fwhm (cm^{-1})	τ (μs)
$\text{Pt}(\text{bpy})\text{Cl}_2$	(641, 250 K)	(4000)	(0.5)	633	2400	3.5
	(624, 77 K)	(2800)	(23)			
$\text{Pt}(\text{bpy})\text{Br}_2$	667	3400	—	—	—	—
	(667, 77 K)	3200				
$\text{Pt}(\text{bpy})\text{I}_2$	695	2650	5.62	695	2300	30.7

Figure 2.8 Emission spectra for microcrystalline samples of (a) Pt(bpy)Br₂ at room temperature (lower intensity spectra) and 77 K; (b) Pt(bpy)I₂ at room temperature (lower intensity spectra) and 10 K (λ_{ex} =457.9 nm). The anomalous structure from 12-14000 cm⁻¹ in the room-temperature spectrum of Pt(bpy)Br₂ is an artifact.

(a)



(b)



As noted previously,²³ the spectrum of Pt(bpy)Cl₂ is strikingly similar to those of Pt(tetramethyl-ethylenediamine)Cl₂ (10 K solid state: λ_{max} , 625 nm; fwhm, 3400 cm⁻¹) and Pt(NH₃)Cl₂ (78 K glassy solution: λ_{max} , 590 nm; fwhm, 3500 cm⁻¹). In analogy to these systems, the observed emission from the Pt(bpy)X₂ complexes clearly originates from a lowest ³LF state. Consequently, the maximum strongly shifts to lower energy with decreasing ligand field strength (Figure 2.4). From spectroscopic studies of PtN₂Cl₂ systems, the lowest spin-forbidden d→d transitions are likely to involve promotion of an electron from a dπ(xz,yz,x²-y²) level to the antibonding d_{xy} level. Indeed, these broad emission bands are consistent with a highly distorted excited state.

In contrast to the spectra of the bromo and iodo derivatives, the emission maximum, lifetime and integrated intensity for microcrystalline Pt(bpy)Cl₂ exhibits a pronounced temperature dependence (Table 2.7).²³ For example, the lifetime increases from 0.5 μs at 250 K to a maximum value of 24.3 μs at 70 K; the value decreases sharply to 3.5 μs at 30 K and remains constant over the 10-30 K range. An Arrhenius activation energy of ~2000 cm⁻¹ has been fit to the data; however, an interpretation of this result is not unambiguous. Clearly, a unimolecular thermally activated process cannot account for such dramatic temperature dependence, and some cooperative effect seems likely.²³ A variable temperature structural study, such as that discussed for the red form of this compound in Chapter 3, will help to clarify this situation.

In the absence of resolved vibronic structure, it is not possible to carry out a full Franck-Condon analysis as previously done for the emission spectra of PtCl₄²⁻ and PtBr₄²⁻.^{75,76} However, the spectra in Figure 2.4 were analyzed using a semiclassical formalism of band-moment theory as described by Lax.⁷⁷ In this treatment, the *n*th moment is given by:

$$M^{(n)} = \int (h\nu)^n G(h\nu) d(h\nu) \quad (2.1)$$

where $h\nu$ is the frequency and $G(h\nu)$ is a shape function describing the band. In the case of emission, G is proportional to (emission intensity)/ $(h\nu)^3$ for a given value of $h\nu$. Thus, the integrand and integral in equation 2.1 (for a given value of n) are readily determined for a given emission spectrum. G is effectively normalized by defining $M^{(0)}$ to be 1. Then, the first moment ($M^{(1)}$) gives the mean frequency of the emission band ($h\bar{\nu}$). For the second and higher moments, it is convenient to redefine G by shifting the origin to $h\bar{\nu}$. Using equation 2.1, the second moment gives the breadth of the emission band ($\sim$ fwhm).

We make the simplifying assumption of Huang and Rhys⁷⁸ that all distortional modes have the same frequency ($\hbar\omega$). (Alternatively, a single distortional mode is assumed to be dominant.) Then, at low temperature the first and second moments are given by:

$$M^{(1)} = E_{0,0} - (\hbar\omega)S \quad (2.2)$$

$$M^{(2)} = (\hbar\omega)^2 S \quad (2.3)$$

where $E_{0,0}$ is the energy gap between the lowest vibrational levels of the ground and excited state potential wells and S is the Huang-Rhys ratio ($I_{1,0}/I_{0,0}$).⁷⁸ Though higher moments also are functions of $E_{0,0}$, $\hbar\omega$ and S , their values are experimentally less accurately determined; consequently, reasonable parameters could not be derived using these expressions. Thus, there are three unknowns ($E_{0,0}$, S , $\hbar\omega$), but only two equations. Since the dominant excited-state distortion is expected to involve lengthening of the Pt-ligand bonds, $\hbar\omega$ is estimated from the average of the Pt-N and Pt-X stretching frequencies (ν_{avg}).^{79,80} The resulting values for S and $E_{0,0}$ are summarized in Table 2.8.

The bandshapes of the emission spectra in Figure 2.4 were also simulated by calculating the Franck-Condon factors for a transition between two harmonic potential energy surfaces (Figure 2.9). In the low temperature limit, the intensity (I) of a vibronic line is given by the proportionality:⁶⁸

$$I(v'' \leftarrow v' = 0) \propto \frac{S^{v''}}{v''!} \quad (2.4)$$

where v' is the quantum number of the lowest vibrational level of the excited state (*i.e.*, $v'=0$) and v'' is the quantum number of the vibrational level of the ground state; the energy of this transition is given by product of v'' and the vibrational frequency ν . Suitable values of simulation parameters are summarized in Table 2.8. The simulated and experimental emission spectra of the Pt(bpy)I₂ and Pt(bpy)Br₂ are shown in Figure 2.9.

Table 2.8. Results from Franck-Condon analyses of the 10 K solid-state emission spectra of Pt(bpy)Cl₂, Pt(bpy)Br₂ and Pt(bpy)I₂.

	<u>Band-moment Analysis</u>			<u>Simulations</u>		
	Pt(bpy)Cl ₂ ^a	Pt(bpy)Br ₂	Pt(bpy)I ₂	Pt(bpy)Cl ₂	Pt(bpy)Br ₂	Pt(bpy)I ₂
ν , cm ⁻¹	310	269	204	310	380	204
S	18.1	23.7	24.3	12	11.5	22.3
$E_{0,0}$, nm	483	478	523	521	520	530

^a Based on 77 K glassy solution emission spectrum.

From the diffuse reflectance spectra in Figure 2.6, it appears that the estimated $E_{0,0}$ for each compound using band-moment analysis is slightly larger than expected. Assuming strong electronic coupling between states, $E_{0,0}$ cannot lie at shorter wavelength (higher energy) than the lowest energy absorption band. This discrepancy is most pronounced for Pt(bpy)Br₂ because of the broadness of its emission. If values of $E_{0,0}$ are restricted to upper limits based on the diffuse reflectance spectra (500, 525, 540 nm for Cl, Br, I, respectively), we find larger vibrational frequencies (522, 382, 232 cm⁻¹) and smaller values for S (9.1, 11.7, 19). Difficulties such as these are not uncommon for this type of band-moment analysis.⁸¹ On the other hand, the bandshapes for Pt(bpy)I₂ and Pt(bpy)Cl₂ (10 K) are well simulated using ν_{avg} and a sensible value for $E_{0,0}$ (Figure 2.9). But for the bromo spectrum, frequencies larger than ν_{avg} are necessary for a

reasonable fit using sensible values for $E_{0,0}$ (Table 2.8). Simulations with two frequencies (*e.g.*, $\nu(\text{Pt-N})$ and $\nu(\text{Pt-X})$) did not substantially improve the situation.

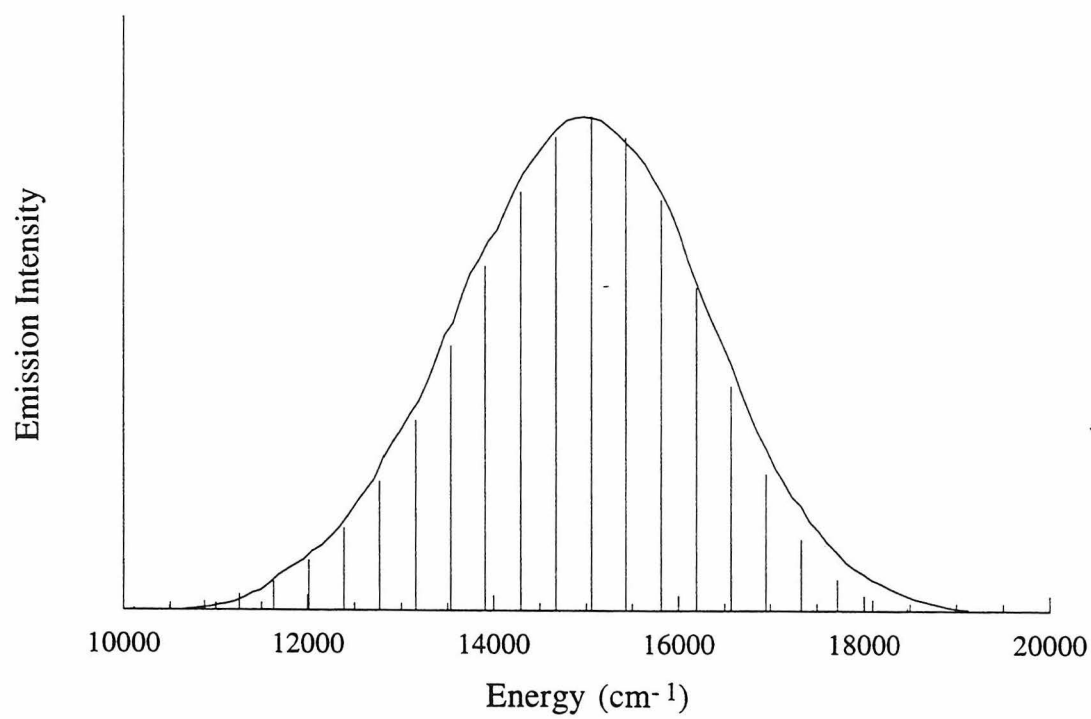
Both the bandshape analysis and spectral simulations give large S values (10-20) that are consistent with a highly distorted excited state. If we assume $\nu'=\nu''$, the change in metal-ligand bond length (Δq) is approximated by^{75,76}

$$\Delta q \approx 8.209 \sqrt{\frac{S}{\mu\nu}} \quad (2.5)$$

(where μ is the reduced mass, approximated by the mass of the halide). We estimate that the Pt-ligand bond lengths increase by 0.2-0.3 Å in the excited state. The estimated $^3\text{d} \rightarrow \text{d}$ absorption maxima ($\sim E_{0,0} + (E_{0,0} - E_{\text{emission maximum}})$) for these complexes are considerably shifted to the blue of the emission maxima, as well as the lowest energy features in the absorption spectrum. This situation is illustrated in Figure 2.10 for $\text{Pt}(\text{bpy})\text{I}_2$. It is intriguing that the simulated absorption spectrum for $\text{Pt}(\text{bpy})\text{Cl}_2$ predicts some intensity at wavelengths longer than the ~475 nm band corresponding to the $^3\pi \rightarrow \pi^*$; in fact, a very broad tail is evident in the diffuse reflectance spectrum for in the 490-510 nm region (Figure 4).

Figure 2.9 Emission spectra and stick diagrams simulating the vibronic intensity pattern for (a) $\text{Pt}(\text{bpy})\text{Br}_2$ (ν , 380 cm^{-1} ; S , 11.5; 520 nm) and (b) $\text{Pt}(\text{bpy})\text{I}_2$ (ν , 204 cm^{-1} ; S , 22.3; 530 nm) at 10 K.

(a)



(b)

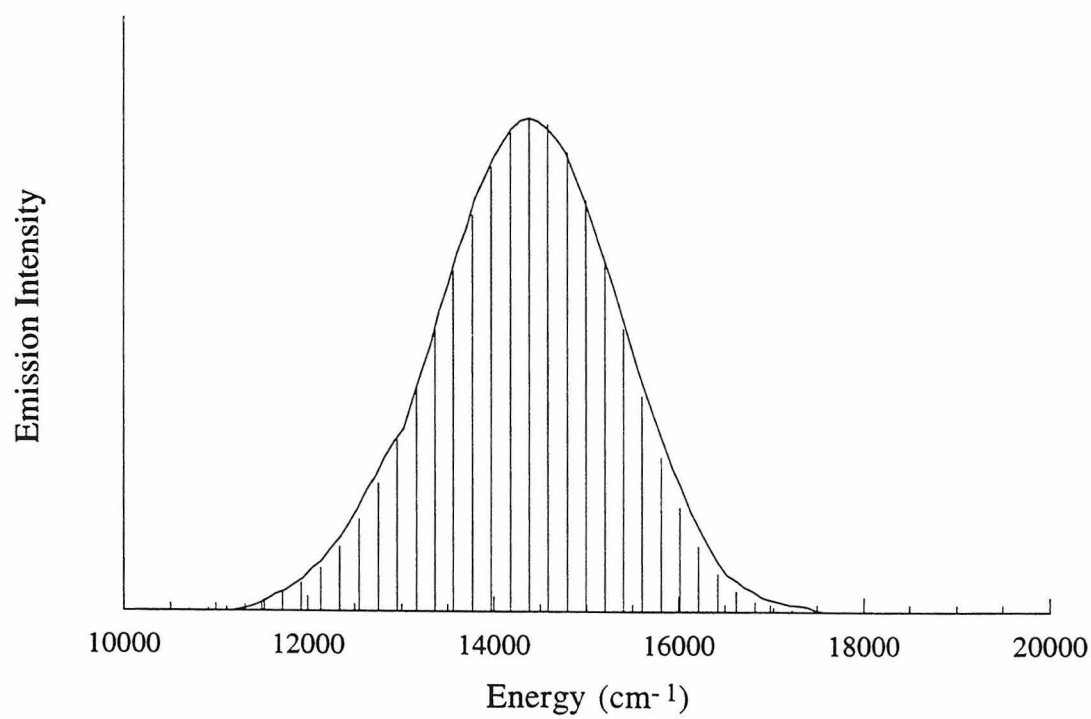
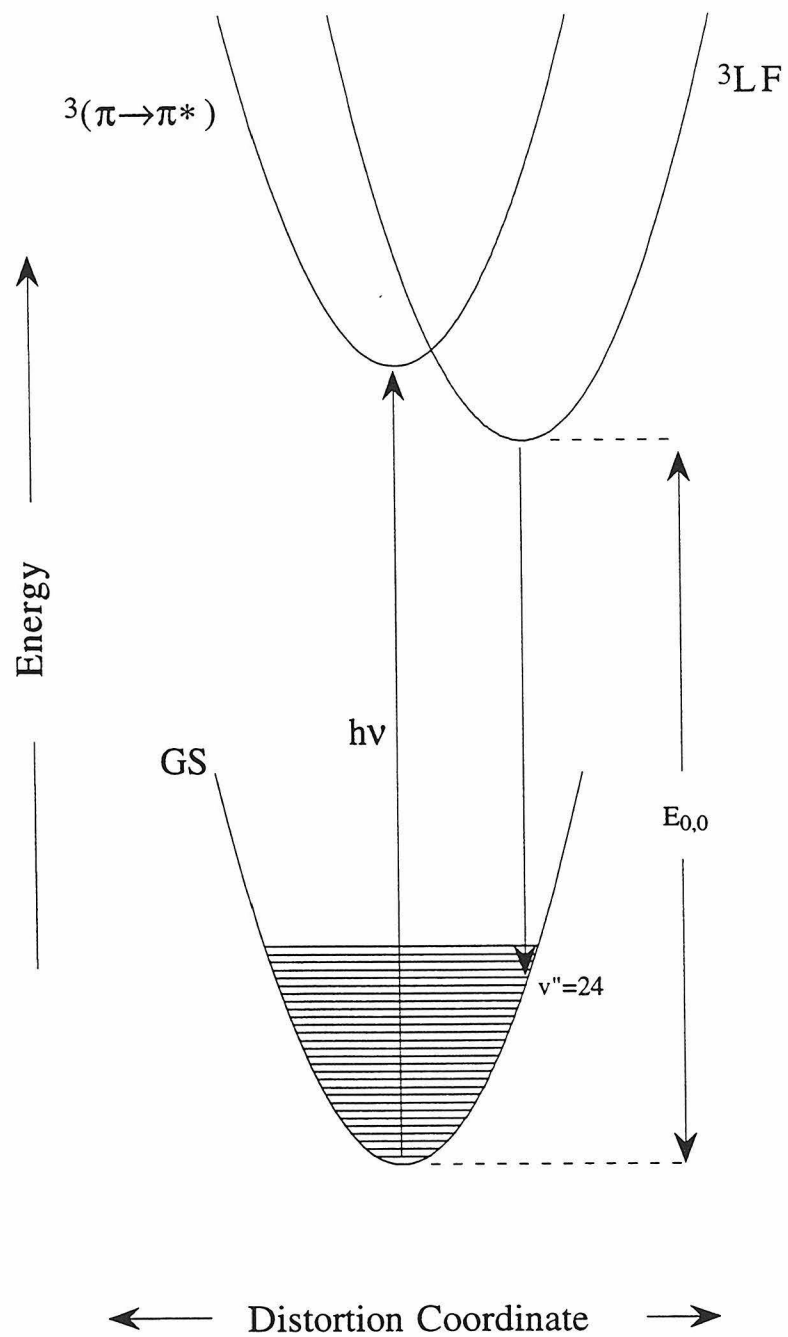


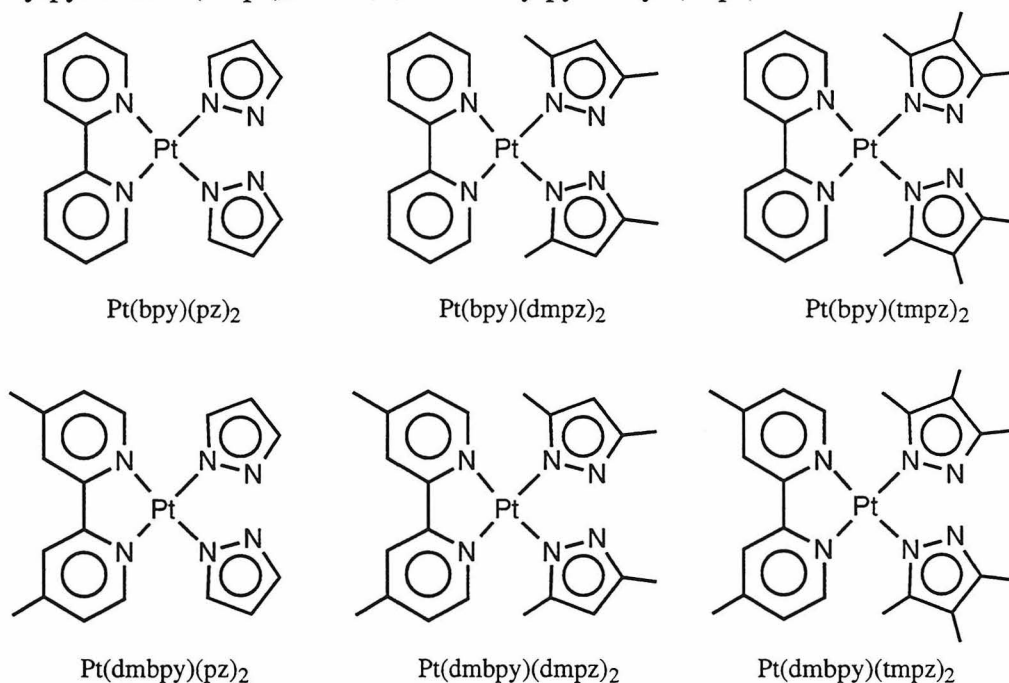
Figure 2.10 Qualitative description of ground-state and excited-state potential energy surfaces for $\text{Pt}(\text{bpy})\text{I}_2$. In this scheme, the minimum of the ^3LF excited-state potential energy surface is shifted along a distortion coordinate with respect to the minimum of the ground-state surface (GS). While the ^3LF state is clearly the lowest state, the vertical transition (Franck-Condon principle) from the ground-state potential energy surface to ^3LF surface *is not* the lowest energy absorption transition. (For example, the maximum for the $^3\pi \rightarrow \pi^*$ band is expected to occur at lower energy than the lowest $^3\text{d} \rightarrow \text{d}$ absorption.) The events leading to the generation of the lowest ^3LF state are not shown, but they may be summarized for a typical case: a photon is absorbed in a spin-allowed process leading to an excited singlet state, subsequent rapid relaxation generates the lowest singlet excited-state, intersystem crossing to the triplet manifold occurs with some probability, and further relaxation gives the lowest triplet state. Since the transition to the ground state is spin-forbidden, this excited state is long-lived (τ , 30.7 μs at 10 K). Because of the relative displacements of the minima of the ground and ^3LF potential energy surfaces, radiative decay results in a characteristically broad emission spectrum with a maximum that is strongly shifted to the red of $E_{0,0}$.



D. Spectroscopy of $Pt(bpy)(pyrazolate)_2$ Complexes

1. Preparation and Characterization

Six monomeric derivatives of bis(pyrazolyl)platinum(II) bipyridyl complexes were prepared by reaction of the appropriate $Pt(diimine)Cl_2$ complex with a potassium pyrazolate salt. These compounds correspond to permutations of diimine ligands, bpy and dmbpy, with the deprotonated pyrazolyl acid derivatives, pyrazolate (pz), 3,5-dimethylpyrazolate (dmpz), and 3,4,5-trimethylpyrazolyl (tmpz):



The compounds form yellow to red-orange air-stable solids. As noted by Minghetti, Banditelli and Bonati,⁴⁷ $Pt(bpy)(dmpz)_2$ is yellow when not completely dry, but orange when dry. $Pt(dmbpy)(dmpz)_2$, and the tmpz derivatives have similar properties. This behavior is reminiscent of the vapochromic properties often exhibited by platinum(II) complexes.^{40,82,83} Analysis of samples which were dried for days at $>80^\circ\text{C}$ under vacuum indicate the presence fewer than 0.5 water molecules per platinum complex. As suggested by the crystal structure of $Pt(dmbpy)(bpy)_2 \cdot (H_2O) \cdot 0.05(thf)$, the tenacity with which these complexes retain water is attributable to the basicity of the pyrazolate ligands. In a previous study of $Ru(bpy)_2(pz)_2 \cdot H_2O$, it was found that the

water of crystallization in this material is tightly held and no anhydrous solid form could be isolated; the pK_a of the conjugate acid $(Ru(bpy)_2(pz)(pzH)^+)$ was estimated to be >13 .⁸⁴ The pK_a of the corresponding platinum(II) complex is probably lower.⁸⁵

The 1H NMR spectra are summarized in Table 2.9. The spectrum of $Pt(bpy)(pz)_2$ is in agreement with the literature, and the other spectra have been assigned accordingly. Methyl substitution at the 4 and 4' positions of the bipyridyl ligand results in a modest upfield shift (0.1-0.2 ppm) in the bipyridyl proton resonances, and only slightly affects the shift of the pyrazolyl resonances. Substitution of the pyrazolyl ligands causes a small upfield shift in the bipyridyl resonances (0.1 ppm); the 6-H position is the most affected, most likely because of a through-space interaction. We surmise from these results that methylation of the pyrazolyl ligand will increase electron density on the platinum.

Table 2.9. Summary of 1H NMR spectra in CD_3OD .

	<u>bipyridine</u>					<u>pyrazolate</u>					
	3-H	4-H	5-H	6-H	4-Me	3-H	5-H	4-H	3-Me	5-Me	4-Me
$Pt(bpy)(pz)_2$	8.40 (d)	8.25 (dd)	7.55 (dd)	8.10 (d)		7.16 & 7.57 (d)		6.11 (dd)			
$Pt(bpy)(dmpz)_2$	8.36 (d)	8.22 (dd)	7.54 (dd)	8.05 (d)				5.63 (s)	1.80 & 2.20 (s)		
$Pt(bpy)(tmpz)_2$	8.35 (d)	8.22 (dd)	7.53 (dd)	8.00 (d)					1.79, 1.81 & 2.15 (s)		
$Pt(dmbpy)(pz)_2$	8.25 (s)		7.35 (d)	7.87 (d)	2.46 (s)	7.14 & 7.54 (d)		6.09 (dd)			
$Pt(dmbpy)(dmpz)_2$	8.21 (s)		7.34 (d)	7.84 (d)	2.45 (s)			5.61 (s)	1.79 & 2.18 (s)		
$Pt(dmbpy)(tmpz)_2$	8.22 (d)		7.34 (dd)	7.81 (d)	2.44 (s)				1.80, 1.81 & 2.13 (s)		

2. Absorption Spectroscopy

These absorption spectra for these compounds are summarized along with their band assignments in Tables 2.10 and 2.11. Spectra for $Pt(bpy)(pz)_2$ and $Pt(bpy)(dmpz)_2$

Table 2.10. Summary of UV-visible spectroscopic data for bipyridyl *bis*-pyrazolato platinum(II) complexes in dichloromethane.

Compound	$^1(\pi \rightarrow \pi_2^*)$	Band II	$^1(\pi \rightarrow \pi_1^*)$	$^1\text{MLCT}$	$^3\text{MLCT(a)}$
Pt(bpy)(pz) ₂	249 [17130]	293 [12160]	321(sh) [6890]	393 [2800]	440(sh) [1430]
Pt(bpy)(dmpz) ₂	251 [22950]	278(sh) [12150]	304, 317(sh) [11960, 9300]	403 [2310]	480(sh) [710]
Pt(bpy)(tmpz) ₂	251 [21780]	(b)	306, 318 [10690, 9450]	392, 440(sh) [1570]	510(sh) [500]
Pt(dmbpy)(pz) ₂	251 [20540]	287(sh) [12840]	318(sh) [7220]	381 [3220]	430(sh) [1580]
Pt(dmbpy)(dmpz) ₂	248, 253 [23250, 23120]	270(sh) [14230]	303(sh), 315(sh) [11290, 8450]	391 [2300]	470(sh) [609]
Pt(dmbpy)(tmpz) ₂	248 [24400]	>270(sh)	302, 315(sh) [10840, 9710]	425(sh) [1291]	490(sh) [450]

^a The $^3\text{MLCT}$ band appears as a shoulder in these spectra, and values of λ_{max} are estimates.

^b Not observed.

Table 2.11. Summary of UV-visible spectroscopic data for bipyridyl *bis*-pyrazolato platinum(II) complexes in methanol.

Compound	Band I	$^1(\pi \rightarrow \pi_2^*)$	$^1(\pi \rightarrow \pi_1^*)$	$^1\text{MLCT}$	$^3\text{MLCT(a)}$
Pt(bpy)(pz) ₂	220(sh)	248	309, 321(sh)	367	420(sh)
	[21410]	[18650]	[9300, 10980]	[2380]	[700]
Pt(bpy)(dmpz) ₂	231	244(sh)	298(sh), 308, 319	379	440(sh)
	[23010]	[21800]	[8290, 10520, 11950]	[1780]	[470]
Pt(bpy)(tmpz) ₂	~241(c)	~241(c)	298(sh), 307, 319	400(sh)	460(sh)
	[26790]	[26790]	[8330, 11200, 12900]	[1230]	[400]
Pt(dmbpy)(pz) ₂	220(sh)	248	395(sh), 306, 318	362	400(sh)
	[27420]	[21720]	[8500, 9630, 11610]	[2780]	[1240]
Pt(dmbpy)(dmpz) ₂	226	244(sh)	295(sh), 304, 317	370(sh)	(b)
	[27250]	[24170]	[7950, 10550, 12890]	[1821]	
Pt(dmbpy)(tmpz) ₂	230(sh)	240	294(sh), 305, 317	390(sh)	440(sh)
	[26920]	[28440]	[8000, 10830, 12790]	[1170]	[420]

^a The $^3\text{MLCT}$ band appears as a shoulder in these spectra, and values of λ_{max} are estimates.

^b Not resolved.

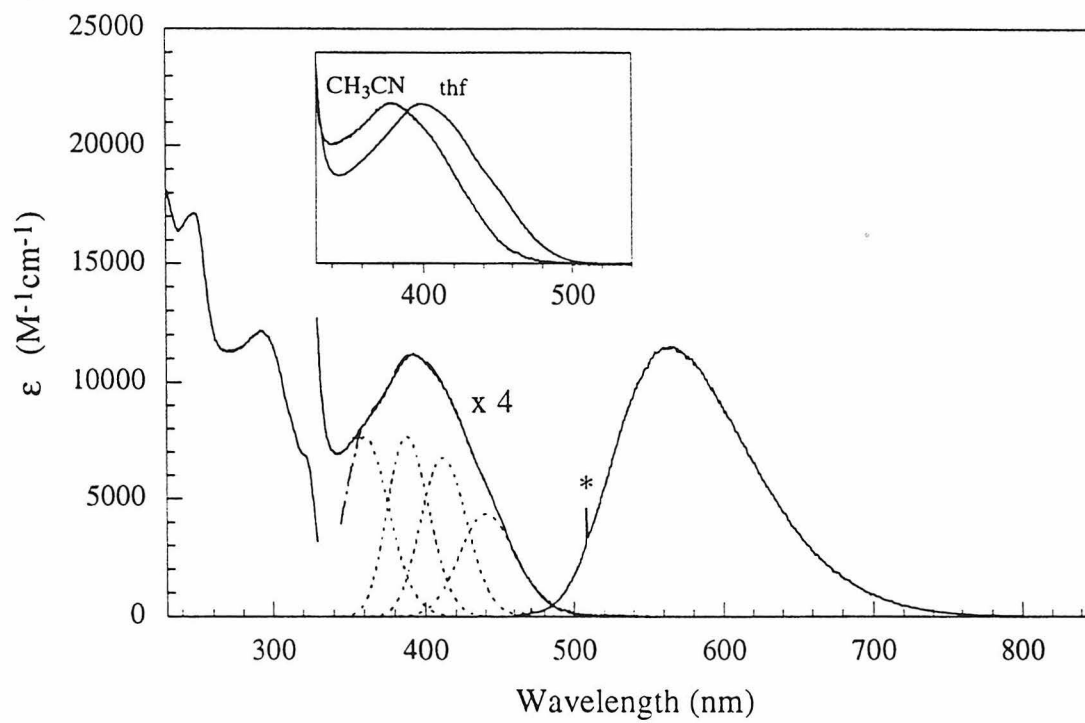
^c Overlapping bands.

are shown in Figure 2.11. In these spectra, the usual $\pi \rightarrow \pi_1^*$ vibronic structure lies near 300-320 nm. However, in methylene chloride these features are not well resolved as a result of overlapping charge-transfer transitions (*vide infra*). A second solvent insensitive band occurs near 250 nm for each complex. This band is assigned to the higher energy spin allowed $\pi \rightarrow \pi_2^*$ transition centered on the bipyridyl ligand. An analogous band is observed in spectra of $\text{Pt}(\text{bpy})\text{Cl}_2^{24}$ and $\text{Ir}(\text{bpy})_3^{2+}$.¹⁰

At longer wavelengths (350-500 nm), there are two bands between 350 and 500 nm that undergo a distinct bathochromic shift with decreasing solvent polarity (Tables 2.10-11; see Figures 2.11-12). The lower energy band is considerably weaker and occurs as a shoulder on the higher energy band. In the case of $\text{Pt}(\text{bpy})(\text{pz})_2$, the maximum of the higher energy feature shifts by 940 cm^{-1} from 379 nm in acetonitrile to 393 nm in dichloromethane (and 399 nm in thf; Figure 2.11a); the $^1\text{MLCT}$ transition of $\text{Pt}(\text{bpy})\text{Cl}_2$ undergoes a comparable shift (800 cm^{-1}). The two bands also shift to lower energy with increasing methylation of the pyrazolyl ligands; a similar shift is observed in the diffuse reflectance spectrum. However, methylation of the bipyridyl ligand induces a slight blue shift. These properties are consistent with both MLCT or LMCT transitions. However, since $\text{Pt}(\text{pz})_2(\text{pzH})_2^{44}$ and $\text{Pt}(\text{dmpz})_2(\text{dmpzH})_2$ are colorless and have no similar low-lying transitions,⁸⁶ thus the possibility of low-lying pyrazolate-localized or pyrazolate $\rightarrow$ Pt charge-transfer transitions are eliminated. In analogy to the $\text{Pt}(\text{bpy})\text{X}_2$ (X=Cl, Br, I) systems, we assign the higher energy band to the transition to a $^1\text{MLCT}$ state and the shoulder at lower energy is assigned to the transition to the corresponding triplet state. From the intensity of the spin-forbidden transition, it is evident that these states are heavily mixed *via* spin-orbit coupling. (For some of these spectra, gaussian deconvolution reveals that there are several overlapping features in the 350-500 nm region; these bands most likely correspond to vibronic structure and/or other MLCT transitions.)

Figure 2.11 Room temperature absorption and uncorrected emission spectra of (a) $\text{Pt}(\text{bpy})(\text{pz})_2$ and (b) $\text{Pt}(\text{bpy})(\text{dmpz})_2$ in dichloromethane solution. Short-dashed lines indicate gaussian components; their sums are shown as long-dashed lines that overlap the absorption spectrum between 320 and 550. Strong dichloromethane Raman lines observed in the emission spectra are marked by an asterisk; weaker lines are present between 460 and 510 nm. The inset in (a) shows the absorption spectrum of $\text{Pt}(\text{bpy})(\text{pz})_2$ in acetonitrile and thf.

(a)



(b)

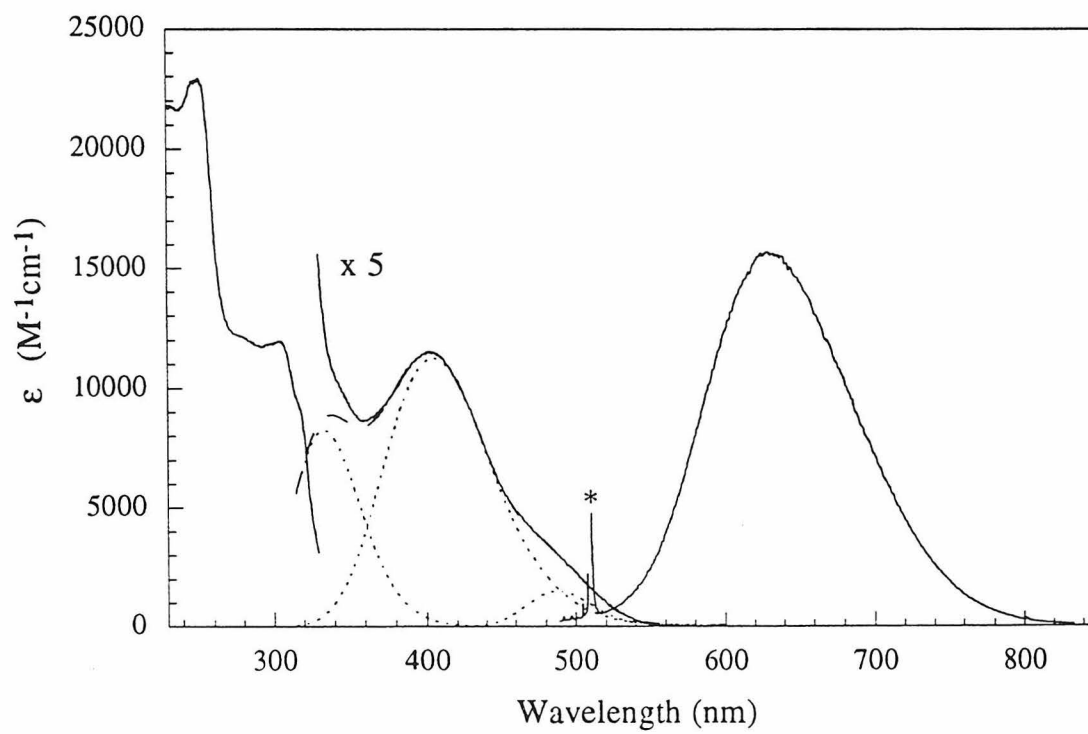
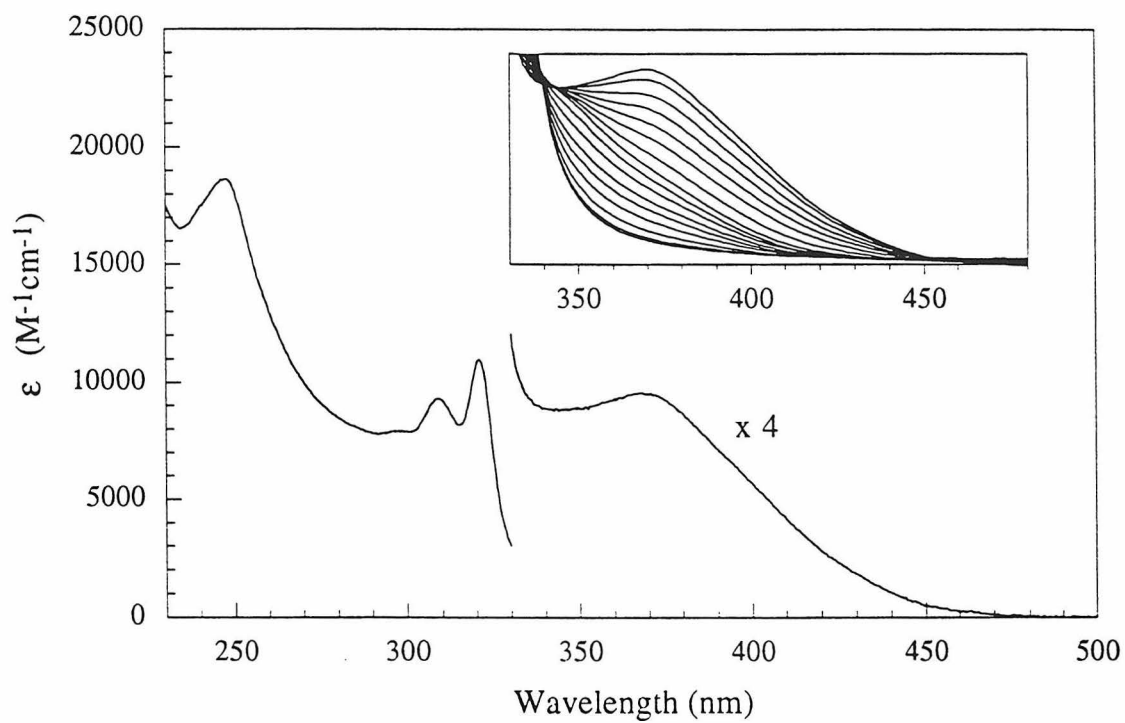
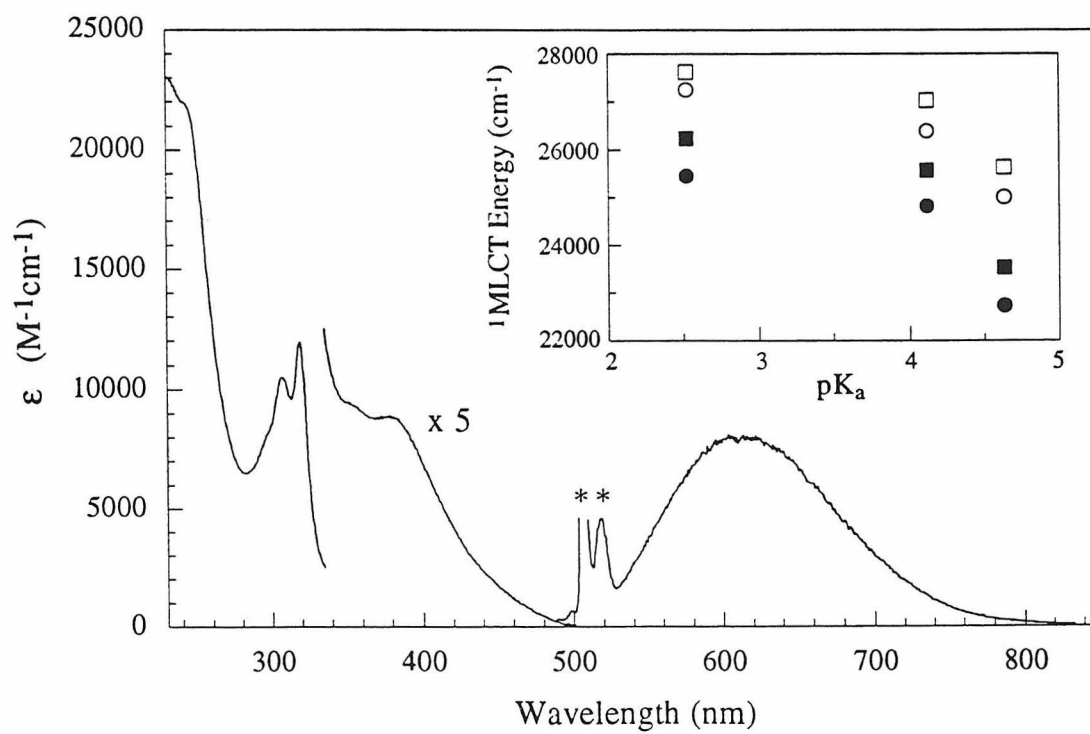


Figure 2.12 Room temperature absorption spectra of (a) $\text{Pt}(\text{bpy})(\text{pz})_2$ and (b) $\text{Pt}(\text{bpy})(\text{dmpz})_2$ in methanol solution. The inset in (a) shows the changes in the absorption spectrum of $\text{Pt}(\text{bpy})(\text{pz})_2$ when titrated with two equivalents of HNO_3 . An isosbestic is observed at 345 nm during addition of the first equivalent, and at 341 nm during the addition of the second equivalent. In (b), the uncorrected emission spectrum of $\text{Pt}(\text{bpy})(\text{dmpz})_2$ in methanol solution is shown; strong methanol Raman lines are marked by an asterisk. The inset in (b) shows the $^1\text{MLCT}$ band maximum for the six platinum(II) diimine *bis*-pyrazolate complexes plotted as a function of the pK_a of the free pyrazolyl acid; pK_a values of pzH , dmpzH , and tmpzH are 2.52, 4.12 and 4.63. The squares refer to complexes containing bpy and the circles refer to complexes containing dmbpy; the solid markers refer to spectra measured in dichloromethane, and the open markers refer to spectra measured in methanol.

(a)



(b)



The 400-800 cm^{-1} blue shift in the MLCT bands arising from methylation of the bipyridyl ligand is attributable to the destabilization of the π^* level; in agreement the reduction potentials of $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{dmbpy})_3^{2+}$ differ by approximately 110 mV ($\sim 900 \text{ cm}^{-1}$).⁸⁷ Similarly, the corresponding red-shift of the MLCT bands with increasing methylation of the pyrazolate ligands is entirely consistent with increasing electron donation to the metal. The ancillary ligands are expected to influence the energy of the MLCT transition primarily by perturbing the metal d-levels. Therefore, electron donation to the platinum center will stabilize this transition. This is consistent with the pK_a values of pzH , dmpzH , and tmpzH which are 2.52, 4.12 and 4.63, respectively (Figure 2.12b).⁸⁸ Conversely, electron-withdrawing groups on the pyrazolyl ligands are expected to destabilize MLCT states. Thus, titration of a methanol solution of $\text{Pt}(\text{bpy})(\text{pz})_2$ with two equivalents of HNO_3 causes the yellow solution to turn colorless because protonation of the pyrazolate ligands induces a dramatic blue-shift of MLCT bands ($\lambda_{\text{max}} < 330 \text{ nm}$) (Figure 2.12a).

The energies of the $^1\text{MLCT}$ transition are similar to those observed for the $\text{Pt}(\text{bpy})\text{X}_2$ series. It appears that the halide and pyrazolate ligands have a similar impact on the energy of the relevant d levels, though the halides are strong π -donors whereas the pyrazolates are strong σ -donors. In fact, from spectroscopic and electrochemical studies it has been suggested that pz is a slightly better electron-donor than chloride. Lever's electrochemical parameterization of ligands shows that Cl^- (-0.24), Br^- (-0.22), F^- (-0.24), and pz (-0.24 V) have similar E_L values, where the reduction potential of a $[\text{Ru}^{\text{III}}(\text{bpy})_n\text{L}_{6-2n}]^{m+}$ complex is given by:⁸⁹

$$E(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}) = 2n(0.255) + (6-n)E_L(\text{L}) \quad 2.4$$

The $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ reduction potential for $\text{Ru}(\text{bpy})_2(\text{pz})_2$ (0.32 V) is 20 mV more negative than the value for $\text{Ru}(\text{bpy})\text{Cl}_2$. Also, the maximum of the MLCT band of $\text{Ru}(\text{bpy})_2(\text{pz})_2$ in dmf lies at slightly lower energy (581 nm) than found for the dichloro analogue (553

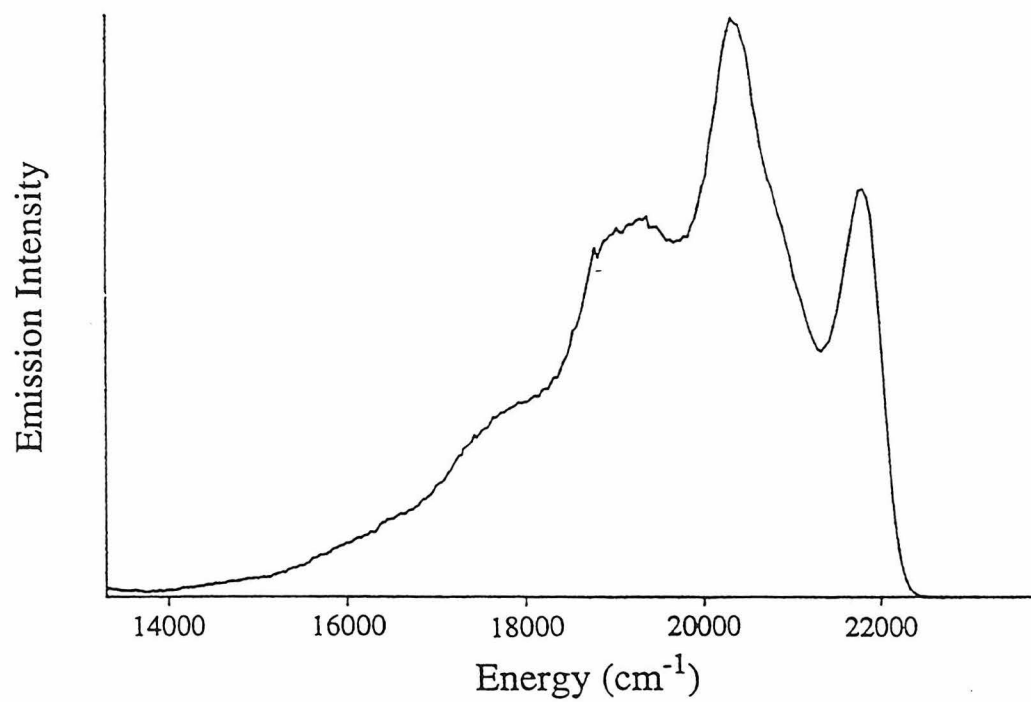
nm).⁸⁴ In the case of these platinum complexes, the strong σ -donor properties of the pyrazolyl ligands tend to stabilize the MLCT states.

The estimated 3000-4000 cm^{-1} splitting of the $^1\text{MLCT}$ and $^3\text{MLCT}$ states is considerably smaller than the bipyridyl $\pi \rightarrow \pi^*$ singlet-triplet gap estimated from absorption spectra of $\text{Pt}(\text{bpy})\text{Cl}_2$ ($\sim 9500 \text{ cm}^{-1}$). Since the singlet-triplet splitting is given by twice the magnitude of the exchange integral, this gap is larger for decreasing spatial separation of the unpaired electrons in the excited state. The $\pi \rightarrow \pi^*$ singlet-triplet gap is comparable to the splitting of $\pi \rightarrow \pi^*$ states in organic molecules, such as anthracene (11580 cm^{-1}).⁹⁰ The magnitude of the MLCT singlet-triplet gap is consistent with an excited state involving charge separation. In classical terms, one unpaired electron resides in the π^* orbital localized on the bipyridyl ligand, whereas the other unpaired electron resides in a metal d orbital. For comparison, MLCT[$d\pi \rightarrow \pi^*(\text{bpy})$] singlet-triplet gap is $\sim 3500 \text{ cm}^{-1}$ for $\text{Pt}(3,3'-(\text{CO}_2\text{Me})_2\text{bpy})\text{Cl}_2$ ²³ and $\sim 2000 \text{ cm}^{-1}$ for $\text{Ru}(\text{bpy})_3^{2+}$.⁶²

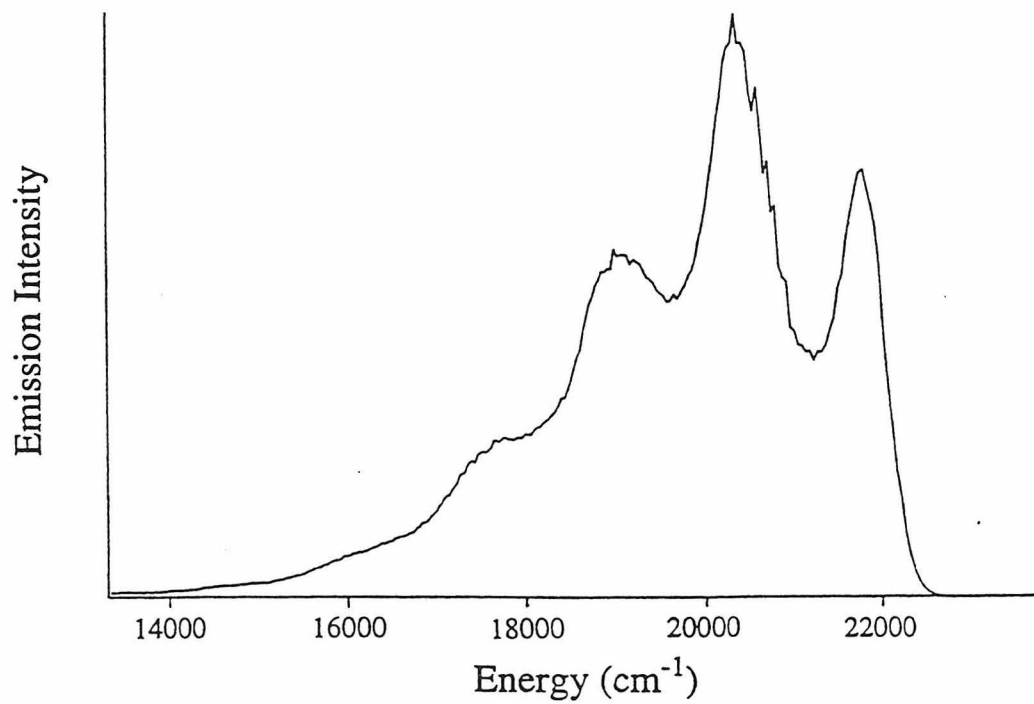
There are several features in these spectra that cannot be unambiguously assigned. Band I is observed in methanol solution spectra at very short wavelengths (220-240 nm). The red-shift of this band with increasing methylation of the pyrazolyl ligands is consistent with a MLCT or LMCT[pyrazolyl $\rightarrow$ Pt] transition. Band II is poorly resolved in dichloromethane solution spectra near 270-290 nm. The apparent blue-shift of this band with increasing pyrazolyl methylation is consistent with the expected behavior of a MLCT[Pt $\rightarrow$ pyrazolyl] transition; however, the energy of this transition is surprisingly low for this assignment. Lastly, in the dichloromethane solution spectra of the methylated pyrazolyl complexes, there is a distinct shoulder near 350 nm. This band is tentatively assigned as a $^1\text{MLCT}$ transition. Further absorption spectroscopic studies are necessary to fully map the excited-state electronic structure of these complexes.

Figure 2.13 Emission spectra for (a) $\text{Pt}(\text{bpy})(\text{pz})_2$ and (b) $\text{Pt}(\text{dmbpy})(\text{pz})_2$ in a 77 K ethanol:methanol (3:1) frozen glass ($\lambda_{\text{ex}}=366$ nm). Emission spectra for microcrystalline samples of (c) $\text{Pt}(\text{bpy})(\text{dmpz})_2$ and (d) $\text{Pt}(\text{bpy})(\text{tmpz})_2 \cdot 0.5(\text{H}_2\text{O})$ at room temperature (lower intensity spectra) and 10 K ($\lambda_{\text{ex}}=457.9$ nm).

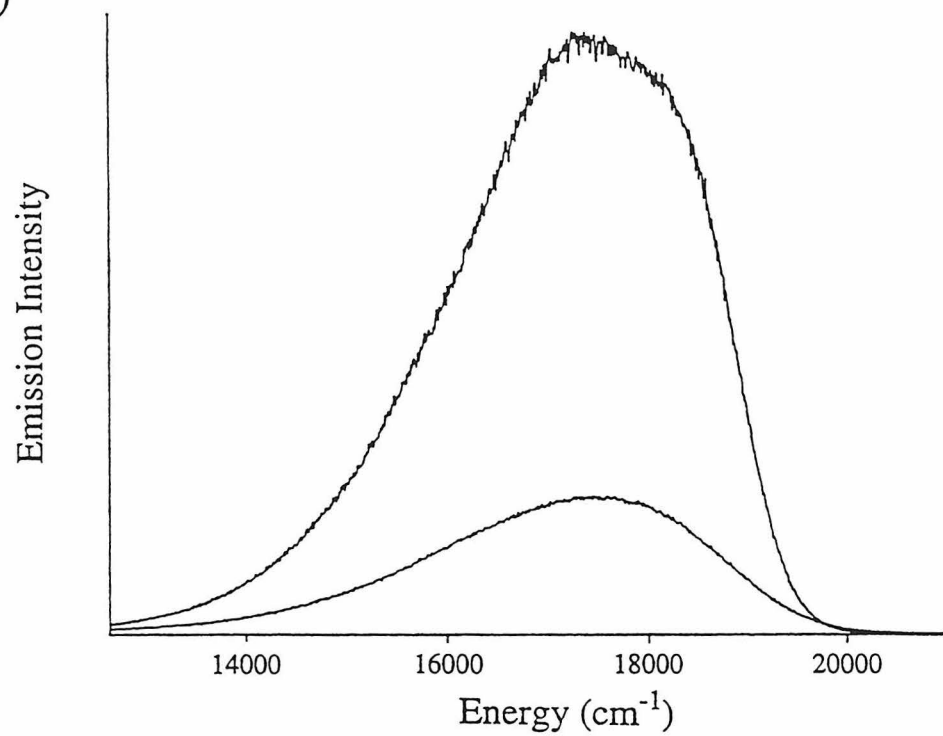
(a)



(b)



(c)



(d)

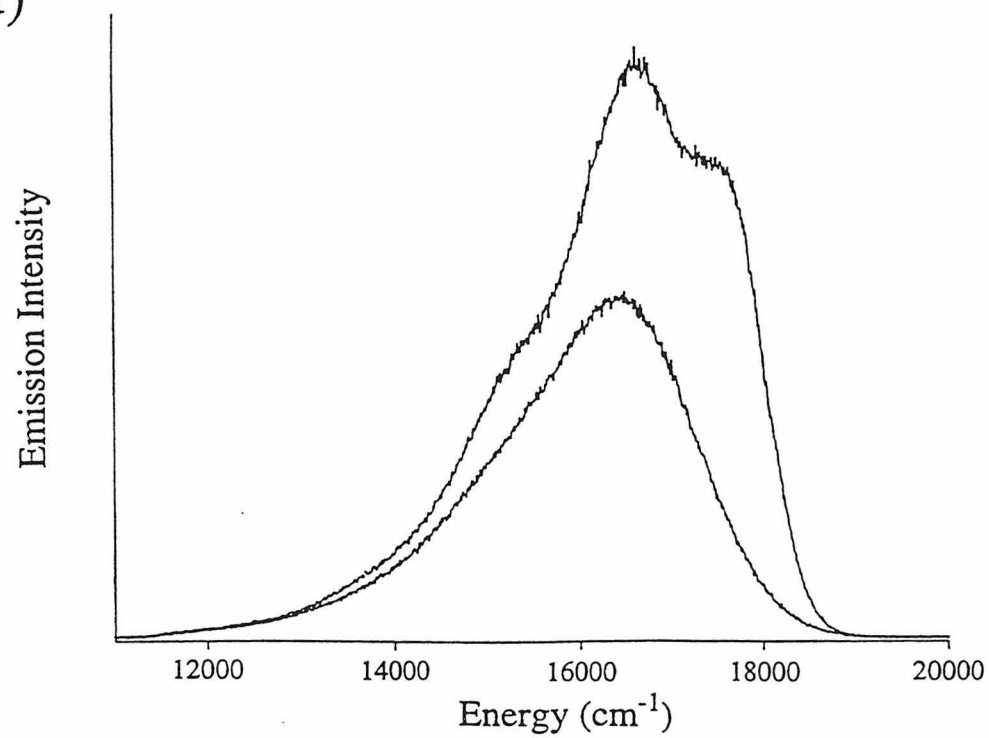


Table 2.12. Summary of emission spectroscopic data for bipyridyl *bis*-pyrazolato platinum(II) complexes.

Compound (emission color)	Emission Band <i>Maxima</i> and Shoulders, nm [τ , ns]			
	<u>Solid State</u>		<u>Glass</u>	<u>Room Temperature Solution</u>
	300 K	10 K	77 K	CH ₂ Cl ₂ Methanol
Pt(bpy)(pz) ₂	481, 509, 549, 588	476, 504, 533, 575	459, 480, 493, 523,	565 —
(yellow-green)	[380]	[3980]	571, 630	[85]
Pt(bpy)(dmpz) ₂	562	568	510	630 612
(orange)	[165]	[585]		[4]
Pt(bpy)(tmpz) ₂	610	654, 602, 570	—	628(a) —
0.5(H ₂ O) (red)	[68]	[140 at 77 K]		
Pt(dmbpy)(pz) ₂	477, 508, 543, 595	478, 513, 549, 595	459, 492, 522,	556 —
(green)			570, 630	[32]
Pt(dmbpy)(dmpz) ₂	573	552, 578,	506	619 588
(yellow)	[210]	[1820]		[7]
Pt(dmbpy)(tmpz) ₂	578	590	—	593(a) —
(H ₂ O) (orange)	[230]	[430 at 77 K]		

^a These solutions are photochemically unstable and the observed emission may originate from a photoproduct.

3. Emission

These complexes are intensely luminescent in the solid state at room temperature and in 77 K glassy solution (Table 2.12). The variation in the color of this emission is striking: the complexes with pz ligands give rise to a green emission, whereas the complexes with methyl-substituted pyrazolyl ligands (dmpz and tmpz) exhibit orange to red emission. The emission spectra for several microcrystalline samples and glassy solutions are shown in Figure 2.13. In room-temperature dichloromethane solution, the compounds are moderately luminescent; however, in methanol they are only weakly luminescent (Figures 2.11, 12b). The tmpz derivatives are photochemically unstable in solution.

The spectra of $\text{Pt}(\text{bpy})(\text{pz})_2$ and $\text{Pt}(\text{dmbpy})(\text{pz})_2$ in frozen methanol-ethanol solution exhibit characteristic $^3\pi \rightarrow \pi^*$ vibronic structure (Figure 2.12). Indeed, these spectra, albeit slightly red-shifted, are very similar to $^3\pi \rightarrow \pi^*$ luminescence spectra of $\text{Zn}(\text{bpy})_3^{2+}$ and $\text{Ir}(\text{bpy})_3^{3+}$.^{8,9} Moreover, the emission profiles are virtually identical with that of $\text{Pt}(\text{bpy})(\text{en})_2^{2+}$ which has vibronic bands at: 459, 481sh, 492, 519sh, 529, and 567sh nm (77 K glass; compare to Table 2.12). Since the green emission from the latter complex clearly originates from a bipyridyl $^3\pi \rightarrow \pi^*$ state,¹¹ the same assignment is made for the pz derivatives in methanol-ethanol glassy solution. The origin (459 nm) of this vibronic pattern overlaps well with the origin of the $^3\pi \rightarrow \pi^*$ band (447 nm) in the absorption spectrum of $\text{Pt}(\text{bpy})(\text{en})_2^{2+}$.¹¹ The fact the emission from bpy and dmbpy complexes are virtually identical indicates that the methyl groups do not significantly perturb the relative $\pi \rightarrow \pi^*$ splitting.

In contrast, the emission from the methyl-substituted pyrazolyl complexes originates from a lowest $^3\text{MLCT}$ state. Close scrutiny of Table 2.12 reveals two important trends: (1) Introduction of electron-donating groups onto the pyrazolyl ligands causes the emission maximum to shift to lower energy and broaden; alternatively, protonation of the pyrazolyl ligands, as in $\text{Pt}(\text{dmbpy})(\text{dmpzH})_2^{2+}$, causes a blue-shift and

results in a highly structured $^3\pi\rightarrow\pi^*$ emission - nearly identical with that of $\text{Pt}(\text{bpy})(\text{en})^{2+}$.⁹¹ (2) In contrast, addition of methyl groups to the bipyridyl ligand causes the emission energy to slightly increase.

We expect the bipyridyl $^3\pi\rightarrow\pi^*$ level to be relatively insensitive to the nature of the ancillary ligands, yet, the emission maximum for $\text{Pt}(\text{bpy})(\text{tmpz})_2\cdot 0.5(\text{H}_2\text{O})$ is $\sim 3000\text{ cm}^{-1}$ lower in energy than the most intense feature in the emission spectrum of $\text{Pt}(\text{bpy})(\text{pz})_2$. A $^3\text{d}\rightarrow\text{d}$ emissive state is ruled out based on ligand field considerations; in fact, the structured $^3\pi\rightarrow\pi^*$ emission from the protonated derivatives establishes that even the lowest $\text{d}\rightarrow\text{d}$ transitions must occur at wavelengths shorter than 450 nm. In addition, the relatively similar broad shape and common origin of the solution, glass, and solid-state spectra for each compound militate against an excimeric emission.¹¹ Finally, since both $\text{Pt}(\text{pz})_2(\text{pzH})_2$ ⁴⁴ and $\text{Pt}(\text{dmpz})_2(\text{dmpzH})_2$ are colorless and do not exhibit similar emission,⁸⁶ pyrazolyl is an unlikely source of this emission. In fact, the behavior described above is similar to that observed for the MLCT absorption bands. Thus, the emission from the complexes with dmpz and tmpz ligands originates from a lowest $^3\text{MLCT}[\text{d}(\text{Pt})\rightarrow\pi^*(\text{bpy})]$ state. Although spin-orbit coupling is clearly significant in these systems, the relatively long solid-state emission lifetimes (70-400 ns) indicate that the emission can be regarded as phosphorescence for the purposes of discussion.

In some instances the distinction between a lowest $^3\text{MLCT}$ or $^3\pi\rightarrow\pi^*$ state is not unambiguous. For example, in the solid state the vibronic structure in the emission spectra of $\text{Pt}(\text{bpy})(\text{pz})_2$ and $\text{Pt}(\text{dmbpy})(\text{pz})_2$ is red-shifted by $600\text{-}800\text{ cm}^{-1}$ from that observed in the spectra of frozen solutions. This result contrasts sharply with the room-temperature solid-state spectrum of $[\text{Pt}(\text{bpy})(\text{en})](\text{ClO}_4)_2$, which is unshifted with respect to the 77 K glass emission spectrum.^{2,11} Thus, while the glassy solution spectra are characteristic of a lowest $^3\pi\rightarrow\pi^*$ state, the solid-state spectra indicate some $^3\text{MLCT}$ contribution. Indeed, the room-temperature emission lifetime for $\text{Pt}(\text{bpy})(\text{pz})_2$ (380 ns) is considerably shorter than that of $[\text{Pt}(\text{bpy})(\text{en})](\text{ClO}_4)_2$ (1400 ns). These results are

consistent with the absorption spectra which show that energy of the $^3\text{MLCT}$ level is very sensitive to the molecular environment; this solvent sensitivity arises from the differences in charge distribution in the ground and excited states.⁹²⁻⁹⁴ Similar spectral changes are seen in frozen solution when using less polar solvents. For example, $\text{Pt}(\text{bpy})(\text{pz})_2$ in 1:1 dichloromethane:toluene solution at 77 K gives rise to the same structured spectrum observed for a methanol:ethanol glass. However, a 1:6 dichloromethane:toluene solution exhibits a broadened and slightly red-shifted emission.

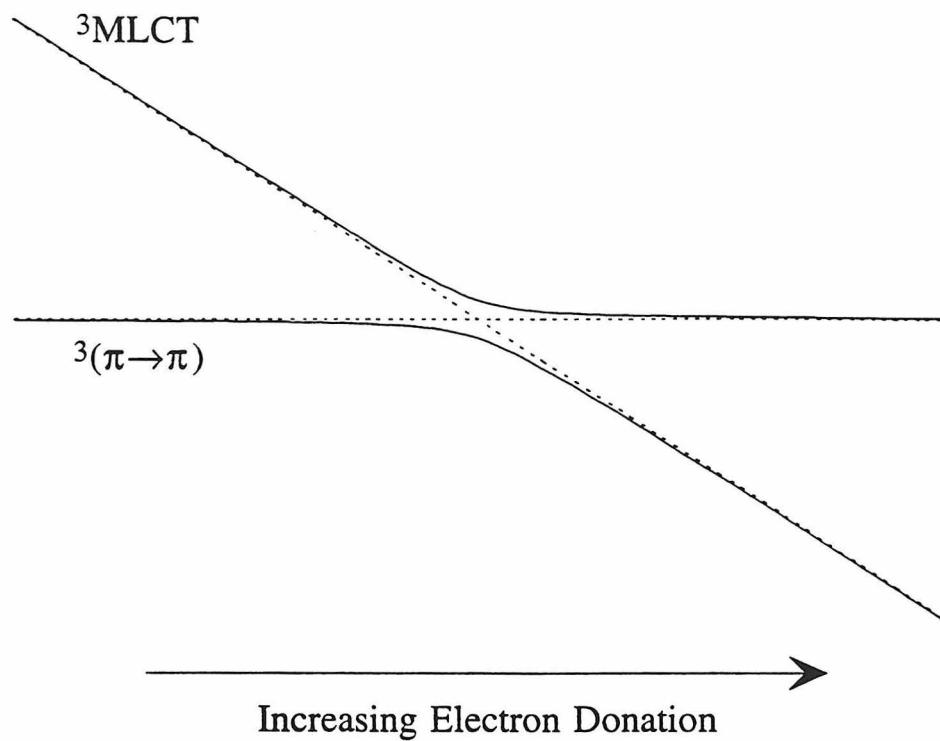
In light of the preceding, it is not surprising that these complexes exhibit luminescence rigidochromism.⁹⁵ The fluid-solution emission is shifted to lower energy with respect to the emission from rigid media, since solvent reorganization tends to stabilize the emissive state. From comparison with related complexes we conclude that the broad asymmetric emission ($\lambda_{\text{max}} \sim 560$ nm) observed for the pz derivatives in fluid solution also originates from a lowest excited state with significant $^3\text{MLCT}$ character. Both $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ ($\lambda_{\text{max}} = 488$ nm, acetonitrile) and $\text{Pt}(4,4'\text{-di-}i\text{-tert-butyl-2,2'-bipyridine})(\text{CN})_2$ (~ 485 nm, $\tau \sim 3$ μs) exhibit structured and blue-shifted emission in fluid solution.^{17,96} The solution luminescence is weak for this series of complexes, and the excited-state lifetimes (τ) are less than 100 ns (Table 2.12). Interestingly, in keeping with our expectation that increased $^3\pi \rightarrow \pi^*$ excited state character results in longer excited-state lifetimes, the complexes with pz ligands have longer lifetimes than those with dmpz.

IV. Conclusion *On the Nature of the $^3\text{MLCT}$ Emissive State*

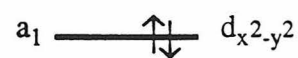
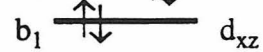
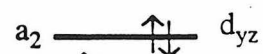
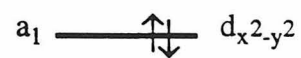
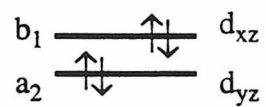
The electronic model which has emerged for the platinum(II) bipyridyl bis-pyrazolates is illustrated in Figure 2.14a. Because we are working with strong-field ligands, the lowest states in these molecules have $^3\text{MLCT}$ and $^3\pi \rightarrow \pi^*$ character. We find that the addition of methyl groups to the pyrazolate ligands lowers the emissive $^3\text{MLCT}$ state below the $^3\pi \rightarrow \pi^*$ state.

Figure 2.14 (a) Energy level diagram illustrating the dependence of MLCT and $\pi \rightarrow \pi^*$ triplet states on the electron-donor properties of the ancillary ligands of a platinum(II) bipyridyl bis(pyrazolate) complex. As the energy gap between these states narrows, mixing of the wavefunctions results produces two states each with substantial MLCT and $\pi \rightarrow \pi^*$ character. (The energies levels were derived by coupling a $^3\text{MLCT}$ wavefunction whose energy (E_{MLCT}) depends linearly on the electron donating parameter (x) and a $^3\pi \rightarrow \pi^*$ wavefunction whose energy ($E_{\pi \rightarrow \pi^*}$) is independent of x .) In (b), ordering of d levels is illustrated for $\text{Pt}(\text{bpy})\text{Cl}_2$.⁹⁷ The d levels may adopt a similar ordering in the $\text{Pt}(\text{bpy})(\text{pz})_2$ complex; another possible ordering, which has been proposed for alkyl complexes, is shown on the right.⁹⁸

(a)



(b)



The exact nature of the emissive MLCT state is an intriguing question. While the predominantly bipyridyl π^* character of the LUMO is well-established in these systems,^{66,70,99-101} the platinum d orbitals comprising the HOMO are less obvious. However, we might expect a somewhat different ordering of d levels than proposed for Pt(bpy)Cl₂ (Figure 2.14); in the latter case, the strong π -donor properties of the halide ligands are expected to strongly destabilize the $d\pi$ levels. In contrast, given the strong σ -donor properties of the pyrazolate ligands, a highest d_{z^2} level is possible. Thus, it seems intuitively reasonable that the emission from the pyrazolate complexes originates from a $^3\text{MLCT}[d_{z^2} \rightarrow \pi^*]$ state.

In fact, Klein and Kaim⁶⁶ have also suggested a lowest $^3\text{MLCT}[d_{z^2} \rightarrow \pi^*]$ state for platinum(II) diimine alkyl complexes. Though we disagree with their proposed ordering of the other occupied d levels,⁹⁸ a highest occupied d_{z^2} orbital is at least consistent with the strong σ -donor capacity of the alkyl ligands. Spectroelectrochemical characterization of the oxidized Pt(diimine)(mesityl)₂ complexes indicates a metal-centered radical; however, even at 4 K no signal could be detected in the EPR (electron paramagnetic resonance) studies. A direct comparison with the pyrazolate complexes is not possible since the Pt(III) pyrazolate complexes are unstable. Conversely, though Pt(diimine)(alkyl)₂ complexes are luminescent in fluid solution, very little photophysical data has been reported.^{30,66} Thus, comparison of the emission properties in these complexes is limited to reported emission maxima; these energies are comparable: dmpz derivatives, ~560 nm in the solid state and ~620 nm in room-temperature dichloromethane solution; Pt(bpy)(mesityl)₂, 610 nm in the solid state and 663 nm in dichloroethane.

Notwithstanding these arguments, a lowest $^3\text{MLCT}[d\pi(xz,yz) \rightarrow \pi^*]$ seems at least equally reasonable. The strong electron-donor properties of the pyrazolate ligands should destabilize all of the d levels by a classical inductive effect, thus it is not certain that the d_{z^2} will lie higher than the $d\pi$ levels. From overlap considerations, we might predict very

weak intensity for the $d_{z^2} \rightarrow \pi^*$ transition - though not zero intensity because of $p_z(\text{Pt})$ - $\pi^*(\text{bpy})$ mixing. Similarly, we expect very different vibronic structure for the $d_{z^2} \rightarrow \pi^*$ and $d\pi \rightarrow \pi^*$ transitions; the $d_{z^2} \rightarrow \pi^*$ transition involves a formally non-bonding (weakly σ -antibonding) metal orbital whereas a $d\pi(xz,yz) \rightarrow \pi^*$ transition involves a π -bonding metal orbital. Yet, the emission profiles of the pyrazolate complexes are conspicuously similar to the ${}^3\text{MLCT}[d\pi \rightarrow \pi^*]$ emission spectra of $\text{Pt}(3,3'-(\text{CO}_2\text{Me})_2\text{bpy})\text{Cl}_2$ and $\text{Ru}(\text{bpy})_3^{2+}$.^{23,102} For $\text{Pt}(\text{dmbpy})(\text{dmpz})_2$ and $\text{Pt}(\text{bpy})(\text{tmpz})_2$ (solid state, 10 K), the Huang-Rhys (S) ratios are estimated to be 1.1 and 1.2, respectively. For $\text{Pt}(3,3'-(\text{CO}_2\text{Me})_2\text{bpy})\text{Cl}_2$, S is approximately 1.05.²³ In contrast, the emission from a ${}^3\pi \rightarrow \pi^*$ state is characteristically sharper with a value of S near 1.3 (*e.g.*, $[\text{Pt}(\text{bpy})(\text{en})](\text{ClO}_4)_2$,^{11,23} $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$,⁹⁶ and $\text{Pt}(\text{bpy})(\text{pz})_2$ in frozen alcohol solution). Therefore, we conclude that a ${}^3\text{MLCT}[d\pi \rightarrow \pi^*]$ assignment seems equally plausible.

We conclude by observing that the reported MLCT emission lifetimes for platinum(II) diimine complexes are relatively short. In the case of $\text{Pt}(3,3'-(\text{CO}_2\text{Me})_2\text{bpy})\text{Cl}_2$, no solution luminescence is detected; however, the solid-state ${}^3\text{MLCT}$ emission lifetimes (350 ns, 300 K; 1100 ns, 10 K) are comparable to the values in Table 2.12.²³ No reliable data is available for the bis(alkyl) systems. As previously suggested,²³ the Pt center is formally oxidized to d^7 in the ${}^3\text{MLCT}$ excited state. Thus, the excited state of the square planar complex may be particularly susceptible to quenching *via* strong interaction with solvent and/or non-totally symmetric distortion. Similar arguments have been invoked to account for the short lifetimes of triplet ligand field states.^{103,104} Both the increased emission intensity in non-coordinating solvents and the increased lifetime in the solid state are consistent with these proposals.

V. References and Notes

- (1) Although spin-orbit coupling is significant in these systems, the spectroscopy and photophysics indicate that there is a clear distinction between singlet and triplet states. Consequently, for the purposes of discussion we treat spin-orbit coupling as a perturbation on the Russel-Saunders coupling scheme.
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the three observed $d \rightarrow d$ transitions for the corresponding Pt(III) complex (600-1600 nm, ϵ 100-600 $M^{-1}cm^{-1}$), the middle transition is *most affected* by changes in the diimine ligand.⁶⁶ The energy of the band increases as E_{red} of the corresponding platinum(II) complexes becomes more positive. The lowest energy transition shows a weaker dependence on E_{red} , and the highest transition correlates poorly with E_{red} . Since the reduction reflects a ligand-centered process, we anticipate the relative dependence on E_{red} to be: $d_{xz} > d_{yz} > d_{x^2-y^2}$. Thus, we arrive at the ordering of d levels: $d_{z^2}(a_1) > d_{yz}(a_2) > d_{xz}(b_1) > d_{x^2-y^2}(a_1)$.

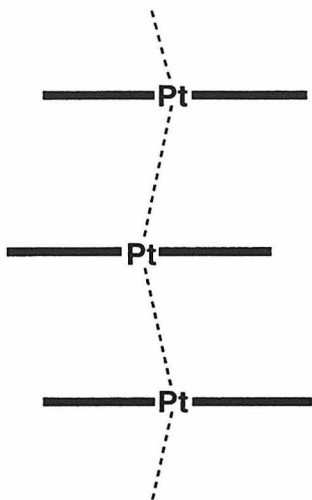
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Chapter 3

Linear-Chain Structures of Platinum(II) Diimine Complexes

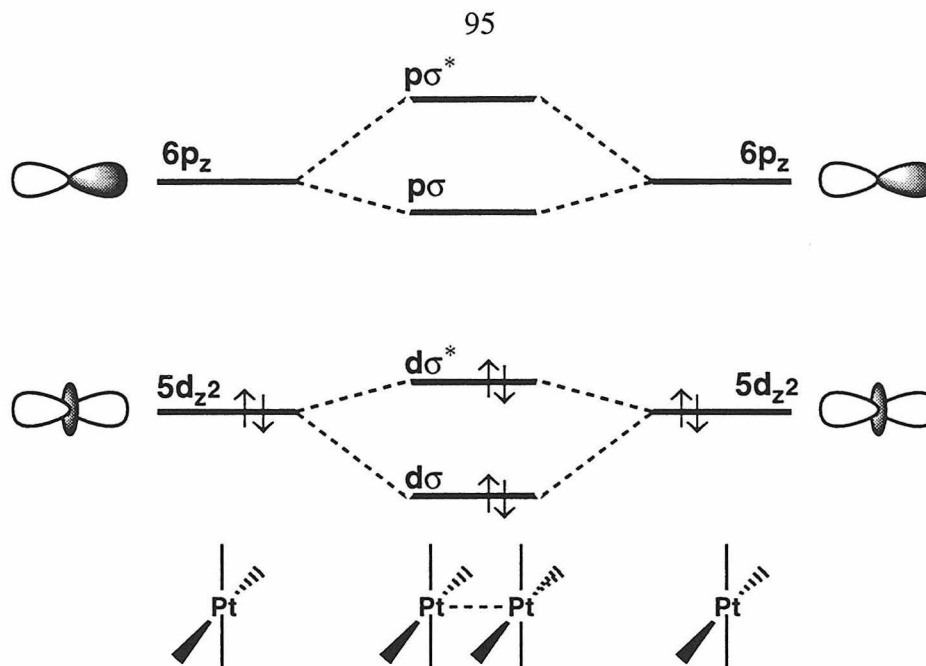
I. Introduction

Square planar platinum(II) complexes often form linear-chain materials with striking spectroscopic properties. In these structures, the planar molecules stack with short Pt...Pt contacts ($< 3.5 \text{ \AA}$), and the Pt...Pt...Pt chain is often slightly zigzag.¹



In analogy to hydrogen bonds,² this weak bonding interaction between d^8 metal centers is a potentially useful tool for the controlled assembly of molecules. In the technical language of crystal engineering, these square planar metal complexes may be regarded as molecular “tectons”³ or “supramolecular synthons”.⁴ In this chapter, we examine the factors governing the stacking of platinum(II) diimine complexes.

The stabilization of these structures is attributable to bonding interactions arising from the overlap of the $5d_{z^2}$ and $6p_z$ orbitals of adjacent metal centers (see below). The fully occupied $5d_{z^2}$ levels of adjacent platinum centers split to give bonding ($d\sigma$) and antibonding ($d\sigma^*$) molecular orbitals; similarly, the unoccupied $6p_z$ levels split to give $p\sigma$ and $p\sigma^*$ orbitals. Since both the $d\sigma^*$ and $d\sigma$ levels are fully occupied, no formal Pt-Pt bonding occurs. However, configuration interaction with the $p\sigma$ and $p\sigma^*$ orbitals stabilizes the $d\sigma^*$ and $d\sigma$ levels, resulting in net favorable interactions.⁵ This description accounts for the solution and solid-state stability, as well as the photophysical properties, of a wide range of stacked complexes with d^8 metal centers, including those of Rh(I), Ir(I), and Pt(II).¹



Because the metal-metal interactions in these systems are relatively weak, the resulting metal-metal distances are often strongly dependent on other factors as well. For example, the metal-metal distance in linear-chain tetracyanoplatinate salts varies from 3.7 to 3.1 Å, depending on the cation and the water content.⁶ Similarly, electrostatic interactions such as in $[Pt(NH_3)_4][PtCl_4]$ (Magnus' green salt),⁷ as well as steric effects, strongly influence the stacking of complexes. Thus, the stacked neutral platinum(II) diimine complexes, which are relatively free of hydrogen bonds and have comparable steric properties, are well suited for investigations of $Pt \cdots Pt$ interactions in the absence of other strong intermolecular forces.

Since the original work on $Pt(bpy)Cl_2$ ($bpy = 2,2'$ -bipyridine) by Osborn and Rogers,⁸ only a few linear-chain platinum(II) diimine complexes have been structurally characterized.^{9,10,11,12,13,14} Obtaining suitable crystals for X-ray diffraction studies is generally difficult, in part due to poor solubility. Moreover, since growth is rapid along the chain axis, samples are typically thin needles and frequently polycrystalline. In this chapter, we report the X-ray crystallographic structures of three linear-chain materials, as well as the structure of the yellow polymorph of $Pt(dmbpy)(NCO)_2$ ($dmbpy = 4,4'$ -

dimethyl-2,2'-bipyridine), which, in contrast to its orange form,^{12,13} has no short Pt...Pt contacts ($< 4 \text{ \AA}$). In addition, a reinvestigation of the structure of $\text{Pt}(\text{bpy})(\text{CN})_2$ demonstrates that a previous study⁹ of this material is incorrect. We also report the temperature dependence of the structure of $\text{Pt}(\text{bpy})\text{Cl}_2$ whose thermochromic properties are discussed in Chapter 4. Our examination of these structures and those of related compounds suggests that the electronic properties of the ligands influence the Pt...Pt interactions.

II. Experimental

A. Materials and Synthesis

Potassium tetrachloroplatinate(II) ($\text{K}_2[\text{PtCl}_4]$), bpy, dmbpy, 1,10-phenanthroline (phen) (Aldrich), 2,2'-bipyrimidine (bpm) (Strem), were used as received. Solvents and other materials were reagent grade unless otherwise noted. $\text{Pt}(\text{bpy})\text{Cl}_2$, $\text{Pt}(\text{dmbpy})\text{Cl}_2$, $\text{Pt}(\text{phen})\text{Cl}_2$,¹⁵ and $\text{Pt}(\text{bpm})\text{Cl}_2$ ¹⁶ were prepared by warming an acidic solution of $\text{K}_2[\text{PtCl}_4]$ and the diimine as described by Morgan and Burstall¹⁷ and later by Bielli and co-workers.¹⁵ A sample of $\text{Pt}(\text{phen})(\text{CN})_2$ was generously provided by V. M. Miskowski.

Potassium ethyl-2-cyano-3,3-dimercaptoacrylate (K_2ecda) was prepared by the method of Jensen and Henriksen.¹⁸ Carbon disulfide (60 ml) and ethylacetate (10.6 ml) were added to a cold (ice bath) mixture of KOH (11.2 g) and tetrahydrofuran (100 ml) under argon. The mixture was stirred for one hour before filtering. The yellow solid was stored in a desiccator.

The following method has proven superior for preparing $\text{Pt}(\text{diimine})\text{X}_2$ complexes, including $\text{Pt}(\text{bpy})(\text{CN})_2$, $\text{Pt}(\text{bpy})(\text{NCS})_2$, $\text{Pt}(\text{dmbpy})(\text{NCS})_2$, $\text{Pt}(\text{phen})(\text{NCS})_2$, $\text{Pt}(\text{bpy})(\text{NCO})_2$, $\text{Pt}(\text{dmbpy})(\text{NCS})_2$, $\text{Pt}(\text{bpy})(\text{N}_3)_2$, $\text{Pt}(\text{bpy})(\text{NCS})_2$, $\text{Pt}(\text{bpm})(\text{NCO})_2$, and $\text{Pt}(\text{bpm})(\text{CN})_2$. In a typical reaction, $\text{Pt}(\text{bpy})\text{Cl}_2$ (0.3484 g) is dissolved in warm dmf (*N,N*-dimethylformamide) or dmsO (dimethylsulfoxide) (~12

ml). The flask is wrapped in aluminum foil to minimize exposure to light. A slightly less than stoichiometric amount (99%) of solid AgNO_3 (0.2785 g) is added to the solution and the mixture is heated for 0.5-1 hour before allowing it to cool to room temperature without stirring. The AgCl is efficiently removed by filtering the solution through a medium frit with celite; on occasion, a second filtration using another frit is necessary. At this point, an excess or slight excess of an appropriate nucleophile (usually dissolved in 1 ml of dmf or water) may be added dropwise to the solution. If the resulting product does not precipitate from solution, excess diethyl ether may be added. The product can be recrystallized from dmf or another solvent.

$\text{Pt}(\text{bpy})(\text{CN})_2$ (**4**) was most easily prepared using the protocol discussed above. Recrystallization from dmf gave orange crystals. Analysis (calc): C, 35.62 (35.74); H, 2.01 (2.00); N, 13.89 (13.89). Alternatively, following the approach of Bielli and co-workers¹⁵ 0.375 g (0.89 mmol) of $\text{Pt}(\text{bpy})\text{Cl}_2$ and 6.5 ml ethylenediamine (en) were combined with 12 ml of water and heated at 50° for three hours. Dropwise addition of a concentrated aqueous solution of NaClO_4 afforded white needles of $[\text{Pt}(\text{bpy})(\text{en})](\text{ClO}_4)_2$. The crystals were washed with aqueous NaClO_4 , toluene, and ether. Initially, the solid produced an orange and yellow emission when exposed to UV light; however, after drying for ~10 minutes on the frit, this emission was exclusively a characteristic yellow-green color. The product was dissolved in cold water (60 ml) and 0.054 g of NaCN (110 mmol) was added to this solution; immediately a yellow precipitate began to form. The isolated product was recrystallized from hot dmf to give orange needles. Analysis (calc): C, 35.79 (35.74); H, 1.89 (2.00); N, 13.80 (13.89).

$\text{Pt}(\text{bpy})(\text{CN})_2 \cdot x\text{H}_2\text{O}$ ^{15,19,20} is reproducibly prepared by cooling a hot pyridine/water (1:1) solution of $\text{Pt}(\text{bpy})(\text{CN})_2$. The yellow plate crystals have a yellow emission; however, their structure is not known. When dried, the crystals return to the orange form (with orange luminescence). The interconversion between the hydrate and anhydrous forms is completely reversible. Bielli and co-workers¹⁵ originally recognized

this behavior and noted that solvent vapors (*e.g.*, HF, H₂O, H₂S) could also effect these color changes. Thus, this vapochromic compound is a well-defined model system for the materials currently under investigation by Mann and co-workers for chemical sensing applications.²¹ Further study of Pt(bpy)(CN)₂ and related compounds is sorely needed; *spectroscopic studies and a crystal structure of the hydrated form should provide direct insight into the mechanism by which these materials respond to solvent vapor.*

Pt(bpm)Cl₂¹⁶ forms an intensely luminescent orange-red solid when precipitated from dmf by addition of diethyl ether. However, crystals grown from dmf or nmp (1-methyl-2-pyrrolidinone) are red. Structural studies of the crystals from nmp solution suggest that this material is composed of Pt(bpm)Cl₂·nmp. The analysis of the bulk material is not consistent with this description; however, no reasonable solvent combination could be found to account for these results. Analysis (calc for C_{10.5}Cl₂H_{10.5}N_{4.5}O_{0.5}Pt): C, 26.24 (26.62); H, 1.93 (2.23); N, 13.07 (13.31); O, 3.99 (1.69); Cl, 17.21 (14.97). On the other hand, elemental analysis of the dried solid was entirely consistent with Pt(bpm)Cl₂. Analysis (calc for C₈Cl₂H₆N₄Pt): C, 22.61 (22.65); H, 1.50 (1.43); N, 13.20 (13.21).

Pt(bpm)(CN)₂¹¹ forms a red crystalline solid with intense red luminescence. Exposure to excessive moisture causes formation of a violet hydrate on the crystal surface.

Pt(bpy)(NCS)₂²² (7) forms fine red needles with an intense red emission. The yellow S-bound isomer, (Pt(bpy)(SCN)₂), is initially formed in the synthesis and exhibits an intense orange emission; however, it was not possible to obtain spectroscopically pure samples of this material because of its tendency to convert to the red form. Analysis found (calc): C, 30.71 (30.83); H, 1.56 (1.72); N, 11.81 (11.99).

Pt(dmbpy)(NCS)₂ precipitates as a yellow solid with an intense orange emission. No red polymorph was observed for this compound. Analysis found (calc): C, 33.26 (33.94); H, 2.13 (2.44); N, 11.25 (11.31).

Pt(phen)(NCS)₂ forms a yellow solid. We did not encounter the red form of this compound by either of the routes suggested by Coyer and co-workers:²³ recrystallization from dmso or heating of the neat solid under vacuum. However, evaporation of a pyridine solution gave a mixture of yellow and red powders.

Pt(dmbpy)(NCO)₂¹² crystallizes in two forms. Orange needles (**1**) and yellow rectangular prisms (**1b**) of Pt(bpy)(NCO)₂ were prepared in roughly equal amounts by slow evaporation of an nmp solution. The two polymorphs were separated using a dissecting needle and microscope with visible or UV illumination of the sample; the yellow crystals (**1b**) are weakly luminescent (green) at room temperature, whereas the orange crystals (**1**) exhibit an intense orange luminescence. Analysis found (calc) for bulk material: C, 35.90 (36.29); H, 2.58 (2.61); N, 12.36 (12.09).

Pt(bpy)(N)₃²⁴ forms both yellow crystals and red needles with a metallic sheen. No visible emission was observed from the red form at room temperature. The red needles were bundles of orange-red fibers which were not suitable for X-ray diffraction studies. This material appears to be photosensitive. Analysis found (calc): C, 27.59 (34.44); H, 1.29 (1.85); N, 25.85 (25.74).

Pt(dmbpy)(ecda) was prepared following the protocol of Zuleta and co-workers.²⁵ We recommend combining a methanol (5 ml) solution of K₂ecda (0.15 g) with a hot acetone solution of Pt(dmbpy)Cl₂ (0.125 g). After boiling for 10 minutes, the mixture should be cooled to 0° C. A mixture of yellow (with orange emission) and red (with red emission) crystals can be grown from acetone or dichloromethane. Crystals grown from CHCl₃ are exclusively yellow. None of the crystals examined were suitable for X-ray crystallography; the red needles were severely twinned.

Pt(bpy)(ecda)²⁵ was prepared in an analogous manner. The yellow solid has a deep orange emission. No unusual solid-state effects were observed.

B. Crystal Preparation

Red crystals of Pt(bpy)Cl₂ (**2**) were grown from a warm pyridine solution (~50°), and orange-red crystals of Pt(bpy)(CN)₂ (**4**) were grown by slow cooling of a hot solution of dmf. In the cases of Pt(bpm)Cl₂, Pt(bpy)(NCS)₂ and Pt(phen)(CN)₂, obtaining crystals suitable for X-ray crystallography studies proved more problematic. For each of these compounds, *numerous* crystals were photographed before a suitable specimen was obtained. Needle-shaped crystals of Pt(bpm)Cl₂·0.5 (nmp) (**3**) were grown by slow evaporation of a solution of nmp. Thin, needle-shaped crystals of Pt(phen)(CN)₂ (**6**) were prepared by slow cooling of a hot dmso solution seeded with crystals from an earlier trial. Blade-like crystals of Pt(bpy)(NCS)₂ (**7**) were grown by vapor diffusion of Et₂O into a dmf (*N,N*-dimethylformamide) solution. Orange needles (**1**) and yellow rectangular prisms (**1b**) of Pt(bpy)(NCO)₂ were readily prepared in roughly equal amounts by slow evaporation of an nmp solution.

C. X-ray Crystallography

In all cases, weights were taken as $1/\sigma^2(F_o^2)$; variances [$\sigma^2(F_o^2)$] were derived from counting statistics plus an additional term, $(0.014F_o^2)^2$; variances of the merged data were determined by propagation of e.s.d.s plus another additional term, $(0.014\langle F_o^2 \rangle)^2$. Atomic scattering factors were taken from Cromer and Waber.^{26,27} Computer programs used were those of the CRYM crystallographic computing system,²⁸ ORTEP,²⁹ XP/PC Molecular Graphics Software,³⁰ and THMA14.³¹ Full details of these structures are available from the Caltech X-ray Crystallography Facility.

1. Variable Temperature Structural Studies of Pt(bpy)Cl₂

A small fragment (0.10 x 0.11 x 0.23 mm) was cut from a needle-shaped crystal and used for all crystallographic studies. Preliminary room-temperature data were

Table 3.1. Crystallographic data for Pt(bpy)Cl₂ at 294 and 20 K.

formula	PtC ₁₀ H ₈ N ₂ Cl ₂
crystal system	orthorhombic
space group	<i>Cmcm</i> (No. 63)
Temperature, K	294 20
<i>a</i> , Å	17.669(5) 17.598(10)
<i>b</i> , Å	9.081(2) 9.059(4)
<i>c</i> , Å	6.804(2) 6.643(3)
Volume, Å ³	1091.7(5) 1059.0(9)
<i>D</i> _{calc} , g/cm ³	2.57 2.65
<i>Z</i>	4 4
No. Reflections	880 1844
No. Reflections <i>F</i> _o ² >0	868 1797
No. Reflections <i>F</i> _o ² >3σ(<i>F</i> _o ²)	804 1714
No. Parameters	48 48
GOF ^a	1.74 2.19
<i>R</i> (<i>F</i> _o >0) ^b	0.0326 0.0340
<i>R</i> (<i>F</i> _o ² >3σ(<i>F</i> _o ²)) ^b	0.0289 0.0317

^a $\text{GOF} = \left(\sum w(F_o^2 - F_c^2)^2 / (n - p) \right)^{1/2}$ where *n* is the number of data and *p* is the number of parameters refined.

^b $R = \sum |F_o - |F_c|| / \sum |F_o|$

Table 3.2. Bond lengths (Å) and angles (°) for Pt(bpy)Cl₂ at 294 and 20 K. Corrected 294 K distances were determined from a rigid-body analysis.^{31,a}

	294 K	294 K (corrected)	20 K
Pt-Cl	2.302 (2)	2.310 (2)	2.308 (1)
Pt-N	2.009 (6)	2.016 (6)	2.015 (4)
N-C(1)	1.350 (10)	1.355 (10)	1.343 (6)
N-C(5)	1.352 (10)	1.357 (10)	1.360 (6)
C(1)-C(2)	1.383 (14)	1.388 (14)	1.383 (7)
C(2)-C(3)	1.358 (15)	1.362 (15)	1.382 (7)
C(3)-C(4)	1.374 (15)	1.379 (15)	1.391 (7)
C(4)-C(5)	1.373 (12)	1.378 (12)	1.382 (7)
C(5)-C(5)'	1.442 (11)	1.447 (11)	1.459 (6)
N-Pt-Cl	95.4 (2)		95.2 (1)
N-Pt-N'	80.2 (2)		80.5 (2)
N-Pt-Cl'	175.5 (2)		175.6 (1)
Cl-Pt-Cl'	89.1 (1)		89.2 (1)
Pt-N-C(1)	125.4 (5)		125.9 (3)
Pt-N-C(5)	114.9 (5)		114.9 (3)
C(1)-N-C(5)	119.8 (7)		119.2 (4)
C(2)-C(1)-N	120.5 (8)		122.0 (5)
C(3)-C(2)-C(1)	120.3 (10)		119.0 (5)
C(4)-C(3)-C(2)	118.8 (10)		119.4 (5)
C(5)-C(4)-C(3)	120.4 (9)		118.9 (4)
C(4)-C(5)-N	120.3 (8)		121.5 (4)
C(5)'-C(5)-N	115.1 (7)		114.9 (4)
C(5)'-C(5)-C(4)	124.6 (8)		123.7 (4)

^a Primed atoms are related by a mirror plane: $-x, y, z$.

collected on an Enraf-Nonius CAD4 diffractometer (MoK_α radiation) with ω scans to a maximum 2θ value of 55° ($\pm h, \pm k, l$). The unit-cell dimensions were obtained from the setting angles of 25 reflections ($19^\circ < 2\theta < 25^\circ$). Throughout this study, diffraction data were corrected for Lorentz, polarization and absorption (Ψ scans of six reflections) effects; the intensity of three standard reflections showed no variations greater than those predicted by counting statistics.

Variable-temperature diffraction data were collected using a modified $\text{P}\bar{1}$ apparatus (MoK_α radiation) designed by Samson and co-workers.³² The temperature was cycled from 294 K (room temperature) to 20 K and back to room temperature; the unit-cell parameters were measured at several intermediate temperatures during both the descending and ascending phases of this cycle. The system was allowed to equilibrate for at least 3 hours before making measurements; the temperature was typically stable to better than $\pm 1^\circ$. The unit-cell dimensions were determined at 294, 200, 100, and 20 K during the cooling phase and at 60, 100, 150, and 294 K during the warming phase; no hysteresis in the reflection intensities or unit-cell dimensions was observed. Cell dimensions were obtained from the setting angles of 28 reflections ($9.5^\circ < \theta < 12.5^\circ$), covering all 8 octants.

Intensities ($\pm h, \pm k, \pm l$) were measured at three different temperatures: 294 K ($2\theta < 60^\circ$), 200 K ($2\theta < 40^\circ$), and 20 K ($2\theta < 81^\circ$). In all cases, the systematic absences (hkl , $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) were consistent with space groups $Cmcm$ (No. 63), $Cmc2_1$ (No. 36) and $C2cm$ (an alternative setting of $Ama2$, No. 40); the structures were successfully refined in the centrosymmetric $Cmcm$. In the case of the room-temperature data set, the Pt atom was located from a Patterson map and the positions of the remaining non-hydrogen atoms were found by successive structure-factor and Fourier calculations. The resulting atomic positions were used as starting coordinates for the refinement of the structure at lower temperatures. Coordinates and anisotropic displacement parameters of all non-hydrogen atoms (as well as a scale factor and

secondary extinction coefficient) were refined at all three temperatures; hydrogen atoms were positioned by calculation (C-H, 0.95 Å) after each cycle of refinement and were assigned isotropic B's 1.15 times that of the attached carbon atoms. Both real and imaginary parts of anomalous dispersion were used in all refinements. Two very strong, low-angle reflections (0 0 2 and 2 0 2) were deleted due to severe disagreement with the final model; these deviations may be symptomatic of uncorrected absorption effects and/or anisotropic secondary extinction. Pertinent data are collected in Table 3.1, and distances and angles are given in Table 3.2.

2. Room Temperature Structural Studies of Linear Chain Complexes

Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer (MoK α radiation and graphite monochromator). Intensities were corrected for Lorentz and polarization effects; data for **1b**, **4** and **6** were corrected for absorption (Ψ scans of six reflections). The intensities of three standard reflections showed no variations greater than those predicted by counting statistics. The Pt coordinates were obtained from Patterson maps, and remaining non-hydrogen atom positions were determined from successive structure-factor, Fourier calculations. Ligand H atoms were positioned by calculation (C-H, 0.95 Å) and were assigned isotropic B's approximately 1.1 times those of the attached carbon atoms. Pertinent experimental data for Pt(bpy)(CN) $_2$ (**4**) are collected in Table 3.3 and bond distances and angles are given in Table 3.4. Pertinent data for compounds **3**, **6**, **7**, and **1b** are summarized in Table 3.5, and selected distances and angles are given in Table 3.6.

Pt(bpm)Cl $_2$ ·0.5(nmp) (**3**). Diffractometer data and Weissenberg photographs indicated that the monoclinic crystal was twinned across the (001) plane; reflections of the type $hk0$ appeared normal, while those with $l \neq 0$ were split. Because β is so close to 90°, the reflections with $l = 1$ were insufficiently separated to be measured independently, and these data were discarded. From the photographs, the two twins

Table 3.3. Summary of crystal data and structure determination information for Pt(bpy)(CN)₂ (**4**).

Formula	PtC ₁₂ H ₈ N ₄
<i>M_w</i>	403.30
Crystal System	orthorhombic
Space Group (No.)	<i>Cmcm</i> (63)
<i>a</i> , Å	18.142(5)
<i>b</i> , Å	9.361(2)
<i>c</i> , Å	6.659(1)
<i>Z</i>	4
<i>V</i> , Å ³	1130.9(4)
<i>D_{calc}</i> , g cm ⁻³	2.369
Crystal Dimensions, mm	0.40 x 0.12 x 0.04
Color	orange-red
Absorption Coefficient, cm ⁻¹	125.17
Extinction ³³	0.18(2) x 10 ⁻⁶
θ-range	1 - 35°
No. Refined Parameters	54
Total No. Independent Reflections	1363
GOF ^a	1.56
No. Reflections (<i>F</i> _{obs} ² > 0)	1287
<i>R</i> (<i>F</i> _{obs} ² > 0) ^b	0.0453
No. Reflections (<i>F</i> _{obs} ² > 3σ(<i>F</i> _{obs} ²))	1096
<i>R</i> (<i>F</i> _{obs} ² > 3σ(<i>F</i> _{obs} ²)) ^b	0.0349
<i>R_w</i> ^c	0.072

^a $GOF = \left(\sum w(F_o^2 - F_c^2)^2 / (n - p) \right)^{1/2}$ where *n* is the number of data and *p* is the number of parameters refined.

^b $R = \sum |F_o - |F_c|| / \sum |F_o|$

^c $R_w = \left(\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right)^{1/2}$

Table 3.4. Bond lengths (Å) and angles (°) for Pt(bpy)(CN)₂ (4).

Pt - N1	2.059(5)	C1 - C2	1.385(11)
Pt - C6	1.949(7)	C2 - C3	1.374(12)
N1 - C1	1.349(9)	C3 - C4	1.373(11)
N1 - C5	1.363(8)	C4 - C5	1.383(10)
N2 - C6	1.152(9)	C5 - C5'	1.448(9)
N1 - Pt - C6	96.0(2)	N1 - C1 - C2	121.6(7)
N1 - Pt - N1'	79.8(2)	C1 - C2 - C3	118.7(7)
C6 - Pt - C6'	88.3(3)	C2 - C3 - C4	119.5(8)
N1 - Pt - C6'	175.7(2)	C3 - C4 - C5	120.9(7)
Pt - N1 - C1	125.7(4)	C4 - C5 - N1	119.2(6)
Pt - N1 - C5	114.2(4)	C5' - C5 - N1	115.9(6)
Pt - C6 - N2	177.7(6)	C5' - C5 - C4	124.9(6)
C5 - N1 - C1	120.2(6)		

Symmetry code: (') -x, y, z

Table 3.5. Crystallographic data for Pt(bpm)Cl₂·0.5(nmp) (**3**), Pt(phen)(CN)₂ (**6**), Pt(bpy)(NCS)₂ (**7**), and Pt(dmbpy)(NCO)₂ (**1b**).

	3	6	7	1b
formula	PtC ₈ H ₆ N ₄ Cl ₂ ·0.5(C ₅ H ₉ NO)	PtC ₁₄ N ₄ H ₈	PtC ₁₂ N ₄ H ₈ S ₂	PtC ₁₄ H ₁₂ N ₄ O ₂
<i>M_w</i>	473.72	427.32	467.43	463.36
color	red	violet	red	yellow
crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	<i>C2/m</i> (no. 12)	<i>Pbca</i> (no. 61)	<i>Pbcm</i> (no. 57)	<i>C2/c</i> (no. 15)
<i>a</i> , Å	12.668(4)	38.731(13)	10.349(3)	17.313(4)
<i>b</i> , Å	15.618(6)	18.569(3)	19.927(5)	12.263(3)
<i>c</i> , Å	6.704(3)	6.628(1)	6.572(3)	14.291(4)
<i>β</i> , °	93.43(3)	—	—	114.00(2)
<i>V</i> , Å ³	1324.0(8)	4766(2)	1355.3(7)	2771.8(11)
<i>D_{calc}</i> , g/cm ³	2.38	2.38	2.29	2.22
<i>Z</i>	4	16	4	8
<i>μ</i> , cm ⁻¹	112.1	118.9	107.4	102.4
no. reflns	978	2213	710	2016
no. reflns <i>F_o</i> ² >0	900	1754	643	1920
no. reflns <i>F_o</i> ² >3σ(<i>F_o</i> ²)	793	1221	565	1605
no. parameters	83	164	67	191
GOF ^a	1.55	1.61	2.80	1.24
<i>R</i> (<i>F_o</i> >0) ^b	0.038	0.069	0.050	0.031
<i>R</i> (<i>F_o</i> ² >3σ(<i>F_o</i> ²)) ^b	0.031	0.041	0.044	0.022
<i>R_w</i> ^c	0.069	0.086	0.099	0.048

^a GOF = $\left(\sum w(F_o^2 - F_c^2)^2 / (n - p) \right)^{1/2}$ where *n* is the number of data and *p* is the number of parameters refined.

^b *R* = $\sum |F_o - |F_c|| / \sum |F_o|$

^c *R_w* = $\left(\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right)^{1/2}$

Table 3.6. Selected bond lengths (Å) and angles (°) for **3**, **6**, **7**, and **1b**.^a

Compound 3			
Pt-N(1)	2.006 (8)	N(1)-Pt-Cl	95.2 (2)
Pt-Cl	2.294 (3)	N(1)-Pt-N(1)'	80.0 (3)
N(1)-C(1)	1.339 (12)	N(1)-Pt-Cl'	175.2 (2)
C(1)-C(1)'	1.463 (13)	Cl-Pt-Cl'	89.6 (1)
Compound 6			
Pt1-N1	2.08 (2)	N1-Pt1-C13	93.8 (11)
Pt1-N2	2.06 (2)	N1-Pt1-N2	81.2 (8)
Pt1-C13	1.95 (3)	N1-Pt1-C14	175.8 (10)
Pt1-C14	1.94 (3)	C13-Pt1-C14	90.2 (12)
C13-N3	1.16 (4)	N2-Pt1-C13	175.0 (10)
C14-N4	1.17 (4)	N2-Pt1-C14	94.8 (10)
N1-C5	1.39 (4)	Pt1-C13-N3	178.5 (3)
N2-C6	1.39 (3)	Pt1-C14-N4	175.8 (3)
Pt2-N5	2.04 (2)	N5-Pt2-C27	96.2 (12)
Pt2-N6	1.99 (2)	N5-Pt2-N6	79.7 (8)
Pt2-C27	1.89 (3)	N5-Pt2-C28	175.3 (11)
Pt2-C28	1.93 (3)	C27-Pt2-C28	88.5 (13)
C27-N7	1.17 (5)	N6-Pt2-C27	175.8 (11)
C28-N8	1.16 (4)	N6-Pt2-C28	95.7 (10)
N5-C19	1.38 (4)	Pt2-C27-N7	176.4 (3)
N6-C20	1.38 (3)	Pt2-C28-N8	174.1 (3)

Compound **7**

Pt-N3	2.06 (2)	N1-Pt-N3	93.5 (8)
Pt-N4	1.91 (2)	N3-Pt-N4	83.1 (8)
Pt-N1	1.94 (2)	N2-Pt-N3	177.4 (9)
Pt-N2	2.11 (3)	N1-Pt-N2	89.1 (9)
N1-C1	1.11 (3)	N1-Pt-N4	176.6 (8)
N2-C2	1.05 (4)	N2-Pt-N4	94.3 (9)
C1-S1	1.68 (3)	Pt-N1-C1	174 (2)
C2-S2	1.57 (3)	Pt-N2-C2	169 (3)

Compound **1b**

Pt-N3	2.005 (5)	N1-Pt-N3	94.6 (2)
Pt-N4	2.001 (5)	N3-Pt-N4	81.2 (2)
Pt-N1	1.985 (6)	N2-Pt-N3	175.4 (2)
Pt-N2	2.007 (6)	N1-Pt-N2	89.9 (2)
N1-C1	1.141 (9)	N1-Pt-N4	175.4 (2)
N2-C2	1.136 (9)	N2-Pt-N4	94.4 (2)
C1-O1	1.203 (9)	Pt-N1-C1	160.2 (6)
C2-O2	1.194 (9)	Pt-N2-C2	153.9 (6)
N3-C8	1.373 (7)	N1-C1-O1	176.9 (8)
N4-C9	1.373 (7)	N2-C2-O2	176.9 (8)

^a Primed atoms are related by a mirror plane: $x, -y, z$.

were estimated to be equal in size, and the intensities of the $hk0$ reflections were halved. The reflections collected for absorption correction were also contaminated by the twinning; loss of the crystal during the January 17, 1994, Northridge earthquake precluded further measurements.

The solvent occupies a region with $2/m$ symmetry; thus, each region has four orientations of an nmp molecule. The positions of the solvent atoms were taken from a difference Fourier map. Several atoms were sufficiently isolated to allow refinement. A difference map in the plane of the solvent at the end of the refinement showed peaks of $1 \text{ e } \text{\AA}^{-3}$ near the N atom positions, but no other peaks so large. Though the C-O distance ($1.25(2) \text{ \AA}$) is reasonable, the B value of the oxygen atoms refined to $0.3(3)$, an unrealistically small number. We can find no chemical or crystallographic reason for this small value.

Pt(bpy)(CN)₂ (4). Preliminary oscillation photographs about the c axis clearly showed weak, odd-order layer lines, confirming that this cell edge must be twice that reported previously (Table 3.7). Data unit cell dimensions were obtained from the setting angles of 25 reflections ($11^\circ < \theta < 13^\circ$); intensities were measured for two separate octants ($+h, \pm k, +l$). Systematic absences were found to be consistent with space groups $Cmcm$ (no. 63), $Cmc21$ (no. 36) and $C2cm$ (an alternative setting of $Ama2$, no. 40); the structure was successfully described in the centrosymmetric $Cmcm$.

Pt(phen)(CN)₂ (6). In addition to the systematic absences characteristic of $Pbca$, the diffraction data exhibit a curious pattern of reflections with $h \neq 4n$ having weak intensity. This observation and the presence of a strong peak in the Patterson map indicate that the Pt atoms are separated by $a/4$. Judicious positioning of the Pt atoms followed by a structure factor and a Fourier map calculation gave the positions of the remaining non-hydrogen atoms. The two molecules in the asymmetric unit are *almost* related by a translation of $1/4$ along x . This pseudo-symmetry results in strong correlation between parameters of atoms in the two molecules (*e.g.*, correlation

coefficients of Pt1, Pt2: x , -0.45; y , -0.67; z , -0.23; N1, N5: x , -0.71; y , -0.68; z , -0.15).

As a result, several C and N atoms could not be refined anisotropically, and therefore, all C and N atoms were refined isotropically.

Pt(bpy)(NCS)₂ (7). The crystal was small and diffracted poorly; only the Pt and S atoms were refined anisotropically.

Pt(dmbpy)(NCO)₂ (1b). A difference map showed that the methyl H atoms are disordered; these atoms were modeled in two orientations in a staggered arrangement. The cyanate ligands were modeled as N-bonded to the Pt. Refinement of the structure with O-bonded cyanate groups gave R (0.0338), $R_{3\sigma}$ (0.0244), and GOF (1.40) values significantly greater than those resulting from refinement of the N-bonded structure; moreover, refinement of the structure with a mixture of N- and O-bonded cyanate also indicated N-bonded coordination [96(5)% Pt-N1-C1-O1; 88(6)% Pt-N2-C2-O2].

III. Results and Discussion

A. Temperature Dependence of the Structure of the Red Form of Pt(bpy)Cl₂

The emission spectrum of the red form of Pt(bpy)Cl₂ is strikingly sensitive to temperature.^{34,35,36} At room temperature, there is a relatively narrow (2000 cm⁻¹ fwhm) and asymmetric band with a maximum at 613 nm; with decreasing temperature, this band sharply narrows and red-shifts, and, at 10 K, the peak is at 651 nm (1050 cm⁻¹ fwhm). This remarkable temperature dependence prompted our structural investigation.

1. Structure at 294 K

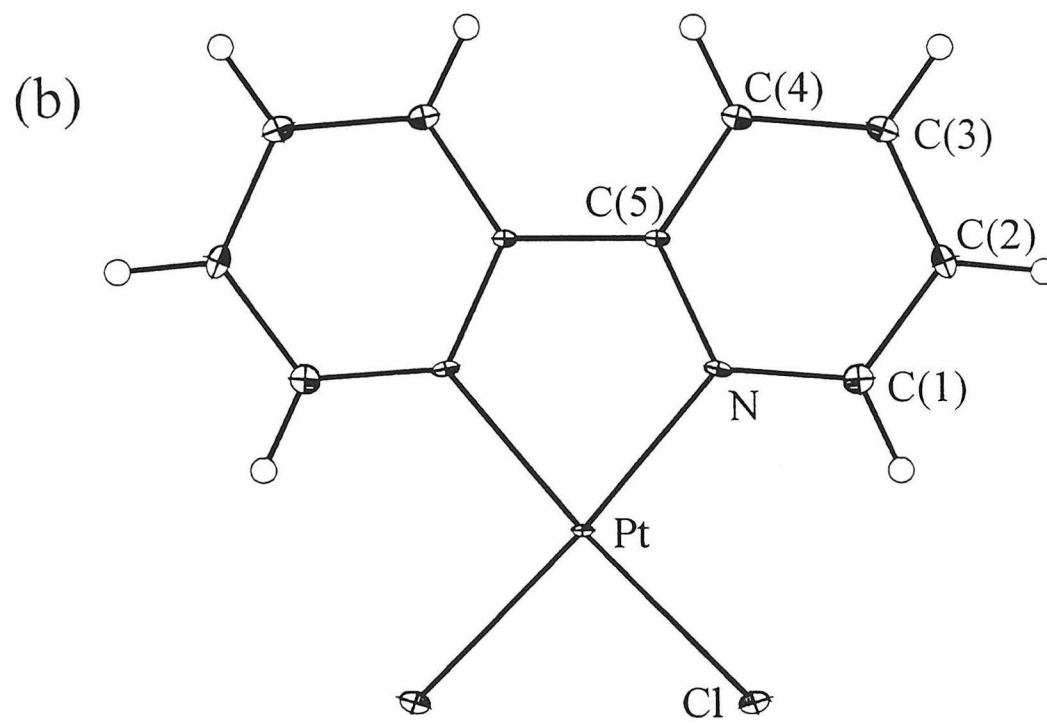
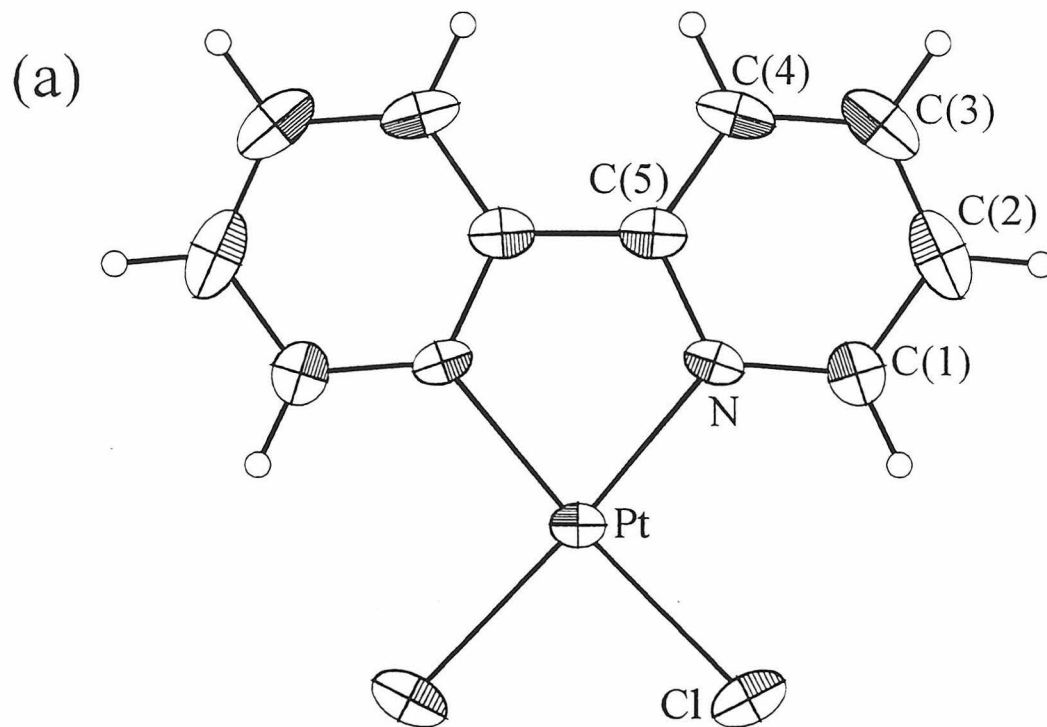
The room-temperature structure reported here and that reported earlier in a study by Osborn and Rogers⁸ are in excellent agreement.³⁷ The unit-cell dimensions, measured three times in this study as well as once previously,⁸ give average values with relatively small scatter standard deviations: $a = 17.669(5)$, $b = 9.085(3)$, $c = 6.802(2)$ Å. Our two room-temperature structures determined using data collected from two different

diffractometers are identical within experimental error; thus, for simplicity, we restrict our discussion to the structure determined from the larger data set.

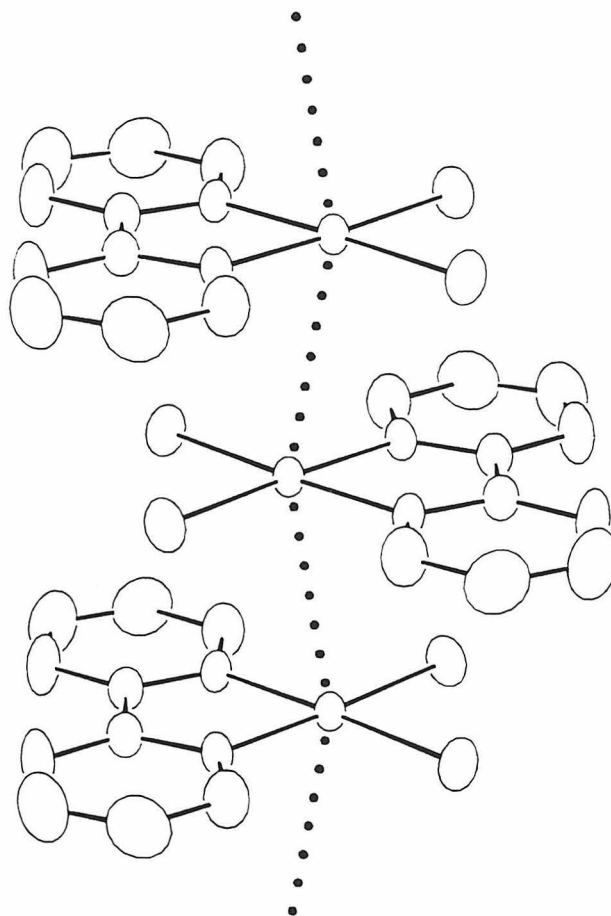
The neutral $\text{Pt}(\text{bpy})\text{Cl}_2$ molecules lie at $z = 1/4$ and $z = 3/4$ and have crystallographic $mm2$ symmetry; the coordination geometry of the platinum is approximately square planar. A drawing of the molecule is shown in Figure 3.1a, and bond lengths and angles are given in Table 3.2. The crystal packing is illustrated in Figure 3.1cd; this arrangement of molecules results in stacking of the complexes to form a chain of planar $\text{Pt}(\text{bpy})\text{Cl}_2$ units with a relatively short interplanar spacing of 3.402(1) Å ($=c/2$). The Pt atoms are displaced by 0.2843(4) Å along b from the chain axis (c), resulting in a Pt...Pt separation between adjacent molecules of 3.449(1) Å and a Pt...Pt...Pt chain angle of 161.03(3)°.

The intramolecular distances and angles are in excellent agreement with those reported for the yellow form of $\text{Pt}(\text{bpy})\text{Cl}_2$.³⁸ The Cl-Pt-Cl (89.1(1)°), N-Pt-N (80.2(2)°) and Cl-Pt-N (175.5(2)°) bond angles are within experimental error of those found for the yellow polymorph (89.1(1); 80.6(4)°; 175.9(3)°, 174.7(3)°).^{38,39} Additionally, the Pt-Cl and Pt-N distances (2.302(2), 2.009(6) Å) are similar to those observed for the yellow form (Pt-Cl: 2.281(4), 2.300(3) Å; Pt-N: 2.006(10), 2.011(10) Å);³⁸ however, the Pt-N bond length is characteristically shorter than reported for structures of complexes such as $\text{Pt}(\text{bpy})(\text{CN})_2$ (2.059(5) Å) that contain strong *trans* σ -donor/ π -acceptor ligands.⁴⁰ The Pt-Cl distance is also nearly identical with values observed for $\text{Pt}(\text{pyridine})_2\text{Cl}_2$ (2.291(5), 2.300(5) Å)⁴¹ and $\text{Pt}(5,5'\text{-dimethyl-2,2'-bipyridine})\text{Cl}_2$ (2.29 Å).^{36,42} Similarly, the geometry of the bipyridyl ligand is in good agreement with that found for related compounds such as $\text{Pt}(\text{bpy})\text{I}_2$.⁴³ Since the distances and angles in the red form accord with a number of platinum structures in which the Pt...Pt contacts are relatively long (>4.5 Å), the stacking interactions do not appear to perturb the molecular structure of the monomeric units.

Figure 3.1 Structure of the red form of $\text{Pt}(\text{bpy})\text{Cl}_2$ at 294 and 20 K. *ORTEP*II²⁹ diagrams with 50% probability ellipsoids showing the geometry of the $\text{Pt}(\text{bpy})\text{Cl}_2$ molecule at 294 K (a) and 20 K (b). H atoms are shown as spheres of arbitrary size. (c) View of the stacking in a single chain of molecules at 294 K; dotted lines indicate the Pt...Pt interactions. (d) View of the crystal packing along the *c* axis and perpendicular to the *ab* plane; the *a* axis is horizontal. H atoms are not shown.



(c)



(d)

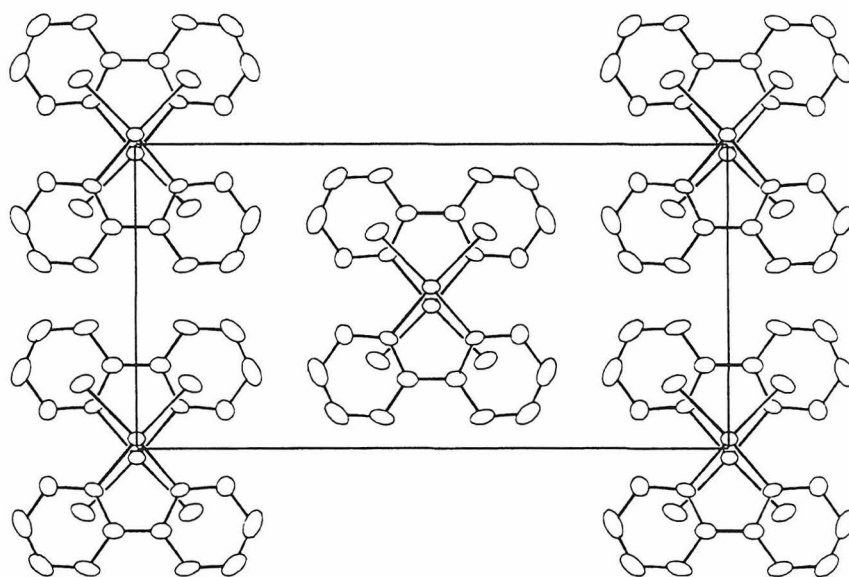
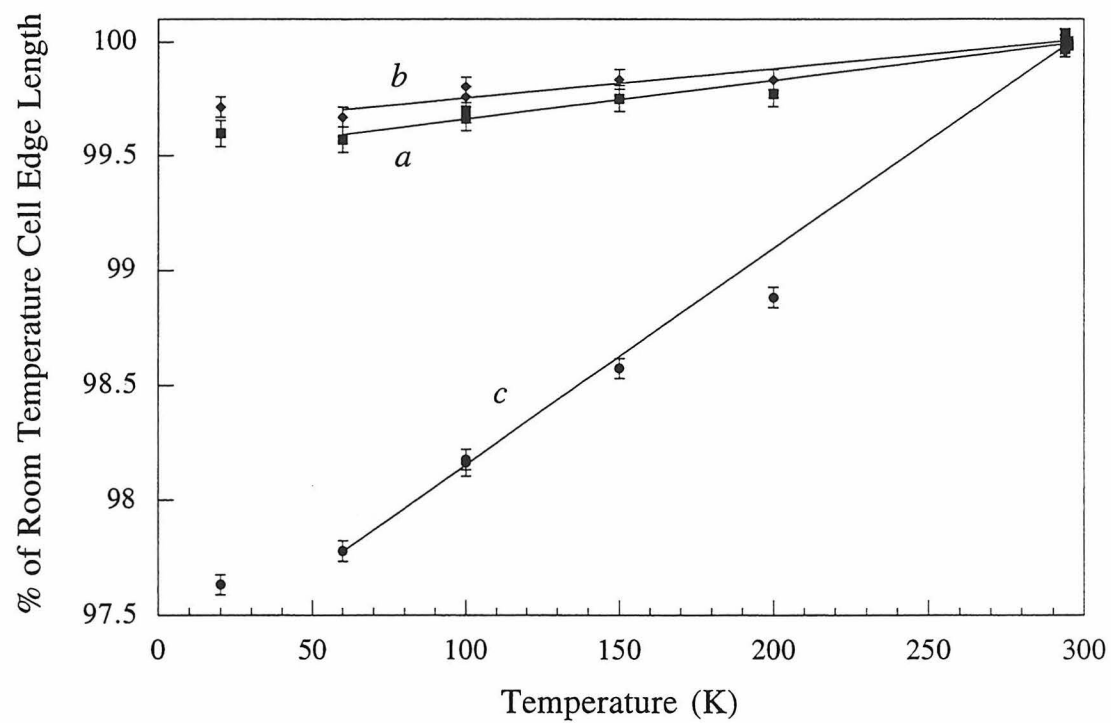
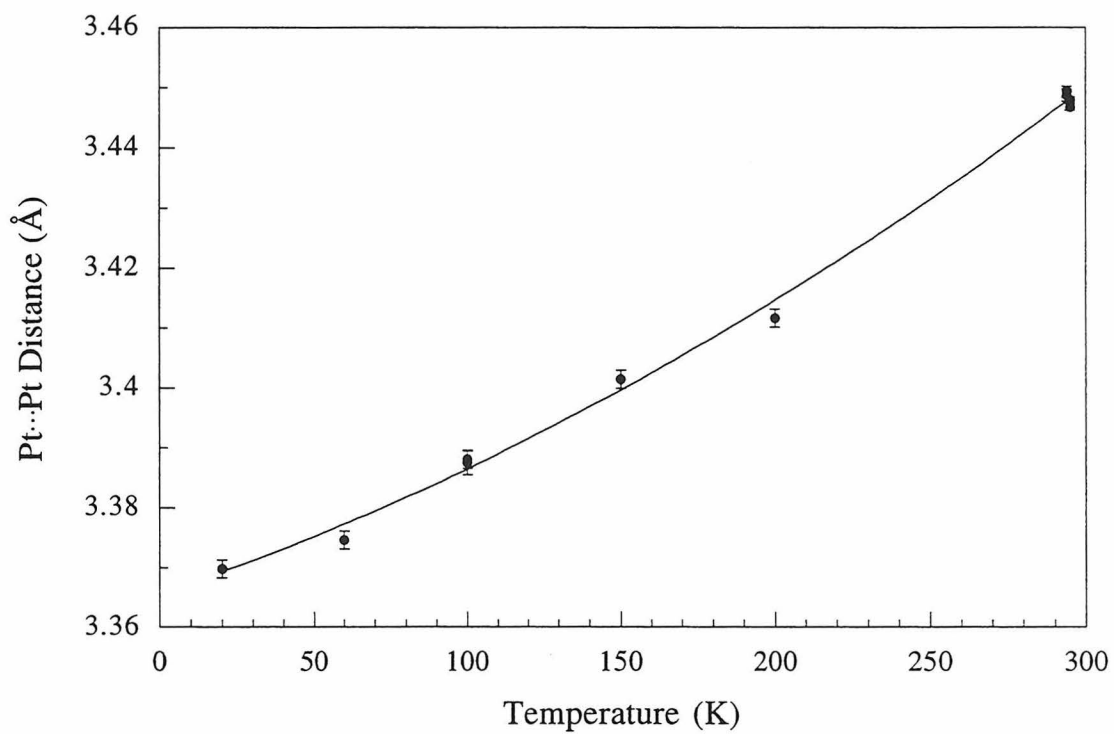


Figure 3.2 Temperature dependence of the structure of the red form of $\text{Pt}(\text{bpy})\text{Cl}_2$. (a) Cell edge length (a , b and c axes) given as a percentage of the room-temperature average value plotted as a function of temperature. Linear fits of data from 295 to 60 K are also shown. (b) Pt...Pt distance plotted as a function of temperature. Five Pt...Pt distances were determined from crystal structures. The remaining five (60, 100, 100, 150, 294 K) were estimated from the unit-cell parameters; the Pt...Pt displacement along z is directly given by $c/2$. The very small, but perceptible Pt y coordinate dependence on temperature was assumed to be linear. The solid line shows the quadratic fit given by eq 3.1. The error bars represent $\pm$ e.s.d.s derived from the unit-cell parameters. In both (a) and (b), the room-temperature measurement from Osborn and Rogers⁸ is included.

(a)



(b)



2. Structure at 20 K

The molecular structure is essentially unchanged at lower temperatures, except for a gradual and slight elongation of the apparent bond lengths and substantially smaller mean-square atomic displacements; thus, we focus our discussion on the structure at the lowest temperature studied (20 K). A drawing of the molecule is shown in Figure 3.1b and distances and angles are given in Table 3.2. On cooling, the bond lengths appear to expand by an average of 0.009(9) Å (scatter e.s.d. given in parentheses) with respect to the room-temperature values; this result is an example of the bond-shortening effect caused by larger librations at room temperature, as noted by Cruickshank.⁴⁴ A rigid-body analysis³¹ of the room-temperature atomic displacement parameters indicates that the bonds should be lengthened by an average of 0.005(1) Å (Table 3.2), bringing them into much better agreement with the low-temperature values. Rigid-body corrections at 20 K are less than 0.001 Å.

As expected, the atomic mean-square displacements (U_{ii}) are markedly reduced with decreasing temperature; the average ratio of the U_{eq} (equivalent isotropic mean-square displacement) at room temperature to the low-temperature value is 1.6(1) at 200 K and 6.4(10) at 20 K. The rigid-body analyses at all three temperatures confirm a gradual decrease in translational and librational molecular motion with decreasing temperature. Interestingly, at all temperatures there is distinct anisotropy in the U_{ii} for Pt (Figure 3.1ab); U_{11} (in-plane) and U_{33} (along the stacking direction) are substantially larger (approximately 3 times at 20 K) than U_{22} (in-plane, along refined coordinate of Pt). The rigid-body analyses support this observation; the mean-square displacements of translational motion (dominated by the Pt) are greater along the a and c axes than along the b axis by almost the same margin. We do not fully understand the reason for this anisotropy.⁴⁵

The most important change in the crystal structure with decreasing temperature is a substantial anisotropic contraction of the unit cell (Figure 3.2a). Upon cooling from

room temperature to 20 K, the lengths of all three unit-cell edges decrease; no hysteresis was observed when the crystal was warmed to room temperature. In addition, there was no evidence of a phase transition over the temperature range studied, although such transformations have been observed in other platinum chain structures.^{46,47} The length of the *c* axis exhibits the greatest thermal sensitivity, decreasing to 97.6% of the room-temperature value at 20 K; the corresponding unit-cell volume is 97.0% of the room-temperature volume. Assuming a linear dependence of thermal expansion over the temperature range from 295 to 60 K (Figure 3.2a), the estimated expansion coefficient along *c* of $9.4(3) \times 10^{-5} \text{ K}^{-1}$ at 295 K is substantially larger than that found along the *a* ($1.7(1) \times 10^{-5} \text{ K}^{-1}$) and *b* ($1.3(1) \times 10^{-5} \text{ K}^{-1}$) axes.⁴⁸ The coefficient of linear thermal expansion of platinum metal is only $0.9 \times 10^{-5} \text{ K}^{-1}$ at 298 K.⁴⁹ However, highly anisotropic thermal expansion is characteristic of both palladium⁵⁰ and platinum linear-chain materials,⁶ and measured expansion coefficients along the stacking axis of tetracyanoplatinate salts range from 8 to $15 \times 10^{-5} \text{ K}^{-1}$ at 295 K.⁶

The cooling-induced contraction of the *c* axis is accompanied by a shortening of the intermolecular contacts between stacked complexes. As there is almost no slippage of the molecules in the *a* or *b* direction with decreasing temperature, the interplanar spacing between stacked Pt(bpy)Cl₂ units matches the contraction of *c* with decreasing temperature. Thus, at 20 K, the intermolecular spacing of $3.322(2) \text{ \AA}$ ($=c/2$) and the Pt...Pt distance of $3.370(2) \text{ \AA}$ are significantly shorter than the room-temperature values of $3.402(1)$ and $3.449(1) \text{ \AA}$. The corresponding Pt...Pt...Pt chain angle of $160.59(4)^\circ$ is approximately 0.4° smaller than at room temperature. Accounting for the small temperature dependence of the Pt *y* coordinate, the Pt...Pt separation was estimated at temperatures for which only unit-cell data are available (Figure 3.2b). The resulting data were fit to a quadratic equation expressing the temperature (*T*) dependence of the Pt...Pt separation (*R*) between 20 and 294 K:

$$R_{\text{Pt}\cdots\text{Pt}} = 3.3657 + 0.000170(T) + 3.72 \times 10^{-7}(T)^2 \quad (3.1)$$

where R and T are in units of Å and K, respectively. Analysis of EXAFS (extended X-ray absorption fine structure) spectra measured at 110 K gave 3.37 ± 0.01 (or 3.36 ± 0.02) Å for the Pt $\cdots$ Pt distance;^{38,51,52} for comparison, the predicted value at this temperature (eq 3.1) is 3.389 Å.

B. Pt(bpy)(CN)₂ - Choosing the Correct Space Group, A Case Study

Though there are many examples of linear-chain materials composed of d⁸ metal centers, we have found few structural reports of Pt(II) diimine compounds stacking to form chains.^{8,9,10,11,12,13} In all but one of these reported structures, successive platinum diimine molecules are rotated by 180° about the chain axis, so that eclipsing of the ligands is avoided and the Pt $\cdots$ Pt $\cdots$ Pt chain is slightly zigzag. The exception to this pattern was platinum(II) bipyridyl *bis*-cyanide (and its palladium analogue, Pd(bpy)(CN)₂), which was reported to crystallize with adjacent molecules exactly eclipsed.⁹ This structure was described in the polar, orthorhombic space group $Cm2m$ (No. 38) with a very short c axis (3.33 Å), and it occurred to us that a doubling of this axis could well lead to the more usual staggered arrangement of stacked complexes along the chain axis. The doubling could occur if systematically weak reflections with l odd had been overlooked in the original investigation: we envisaged a structure, perhaps in space group $Cmcm$, as found for Pt(bpy)Cl₂⁸ and Pt(bpy)(NCO)₂,¹² with successive Pt atoms approximately but not exactly superposed. Our re-investigation of the structure confirmed our suspicion.

This re-investigation also serves as an interesting case study. Though accidental halving of the unit cell will, typically, lead to the conclusion that the structure is disordered, in the present case no disorder was apparent in the original $Cm2m$ structure. This result illustrates that, in certain instances, suspicious disorder arising from halving a

unit cell may be eliminated by refinement in a non-centrosymmetric space group. The resulting model may appear crystallographically reasonable, but is grossly incorrect.

1. Description of Structure

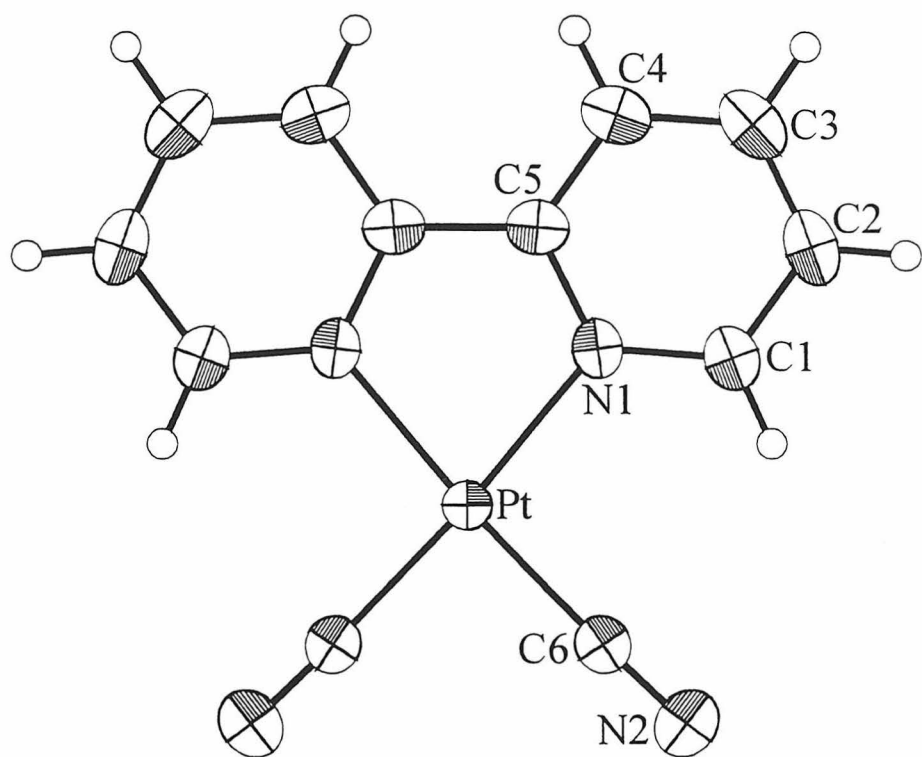
$\text{Pt}(\text{bpy})(\text{CN})_2$ is isostructural⁵³ with the red form of $\text{Pt}(\text{bpy})\text{Cl}_2$. Thus, the neutral molecules lie on mirror planes at $z=1/4$ and $z=3/4$ and have crystallographic symmetry $mm2$; the bonding about the Pt is approximately square-planar. A drawing of the molecule is shown in Figure 3.3a, and bond lengths and angles are given in Table 3.4.

The cyanide ligands are linearly coordinated to the Pt, with a normal C-N bond length of 1.159(9) Å.⁵⁴ The Pt-C distance, 1.949(7) Å, is close to the values 1.92(1) and 1.94(1) Å reported for the related linear chain compound $\text{Pt}(\text{bpm})(\text{CN})_2$.¹¹ The Pt-N(bpy) distance of 2.059(5) Å is also in satisfactory agreement with the values 2.042(8) and 2.057(7) Å found for $\text{Pt}(\text{bpm})(\text{CN})_2$.¹¹

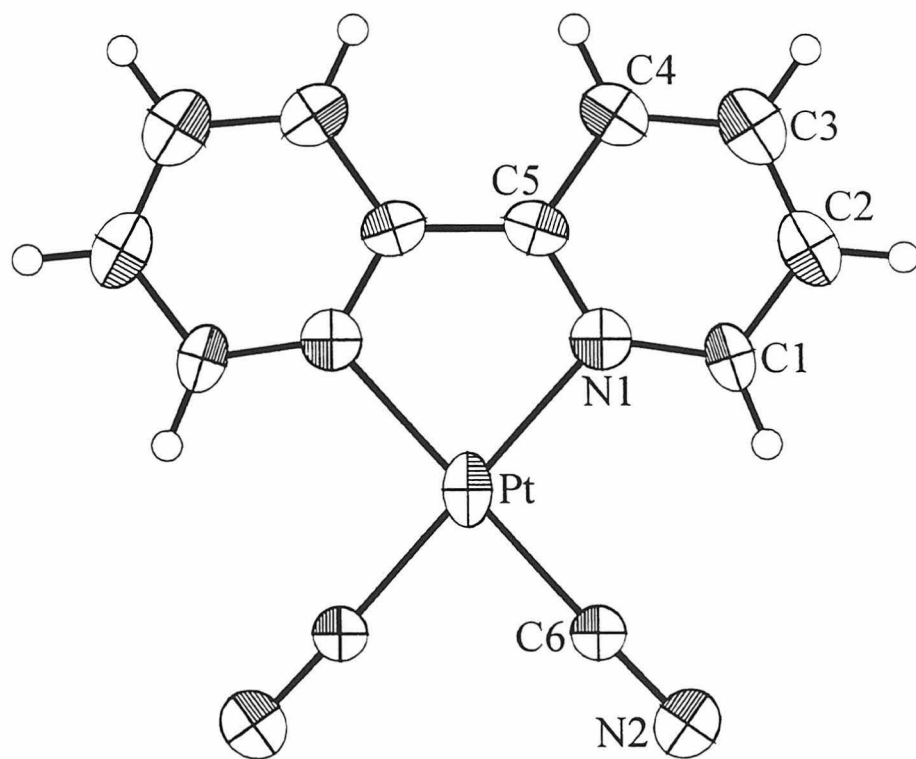
The crystal packing is illustrated in Figure 3.3cd. As in crystals of the red form of $\text{Pt}(\text{bpy})\text{Cl}_2$, the complexes stack along the c axis to form an approximately linear chain of platinum atoms. Consecutive molecules along the chain are related by the c -glide perpendicular to b , and consequently are rotated by 180° about c . This arrangement leads to a staggered, rather than an eclipsed, arrangement of ligands in adjacent molecules while still accommodating relatively close Pt...Pt contacts. The Pt atoms along the chain are slightly offset from the c axis, by 0.1662(3) Å along b , resulting in a Pt...Pt...Pt chain angle of $168.6(1)^\circ$. (It is the proximity of this y coordinate to 0.0 which is responsible for the relatively weak intensities of reflections with l odd - the reflections which were overlooked in the earlier work of Che and co-workers.)⁹ In the red form of $\text{Pt}(\text{bpy})\text{Cl}_2$, the Pt atoms are offset by a slightly greater distance (0.2843(4) Å) and the Pt...Pt...Pt chain angle is $161.03(3)^\circ$. The interplanar spacing between molecules along the chain also is somewhat greater in that dichloro compound (3.40 Å) than in the present dicyano

Figure 3.3 Structure of $\text{Pt}(\text{bpy})(\text{CN})_2$. *ORTEP*II²⁹ diagrams with 50% probability ellipsoids showing the molecule described in space groups (a) *Cmcm* and (b) *Cm2m*. H atoms are shown as spheres of arbitrary size. (c) View of the stacking in a single chain of molecules; dotted lines indicate the Pt...Pt interactions. (d) View of the crystal packing along the *c* axis and perpendicular to the *ab* plane; the *a* axis is horizontal. H atoms are not shown.

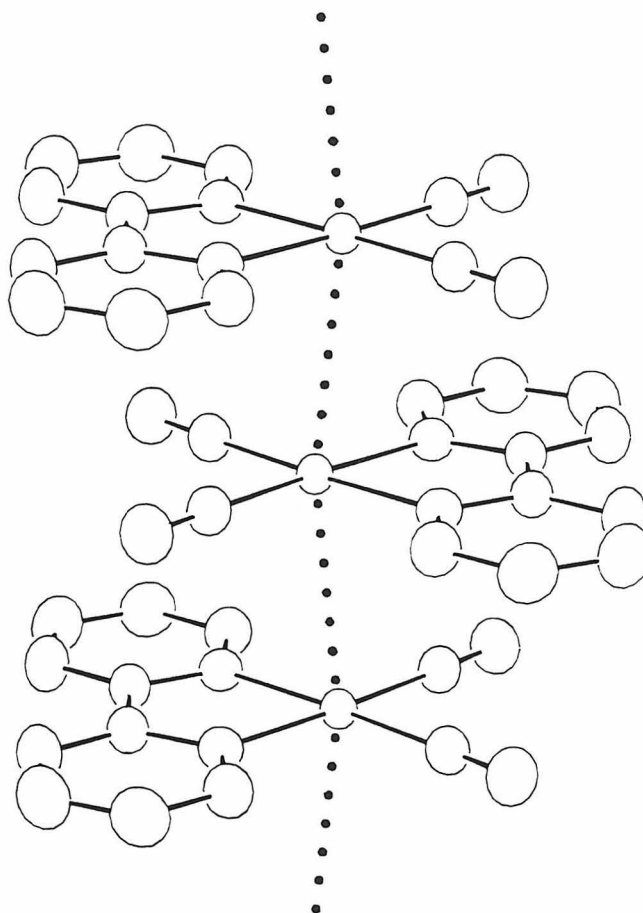
(a)



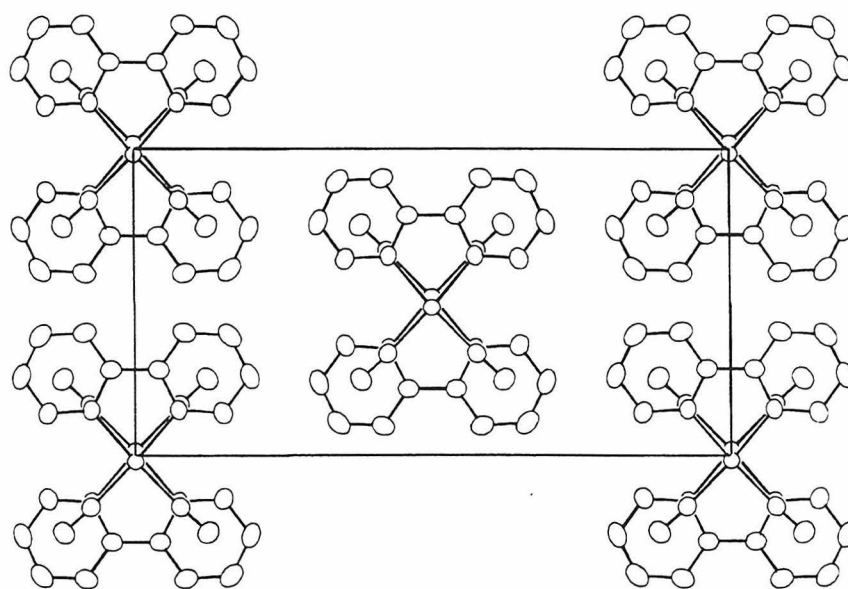
(b)



(c)



(d)



compound (3.33 Å), and the resulting Pt...Pt distance is appreciably greater: 3.449(1) vs. 3.3461(5) Å.

2. The Earlier Structure: What Went Wrong?

The structure reported by Che and co-workers⁹ was based on a unit cell half as large (Table 3.7). Reflections with l odd, which are systematically weak because of the nearly-linear arrangement of Pt atoms, were apparently overlooked during the diffractometer search for orienting reflections. Such events have surely occurred before.^{55,56} The usual result is that the incorrect structure, based on too small a unit cell, is disordered; in effect, the two molecules in each stack shown in Figure 3.3d must be superposed in order to create the appearance of a smaller cell. In the present case, however, the structure reported by Che *et al.*⁹ seemed to show no such disorder; the only hint of possible trouble was a somewhat large and elongated (along b) U_{ij} ellipsoid for the Pt atom and, perhaps, some slightly peculiar bond lengths and angles. Why was there no apparent disorder?

Table 3.7. A comparison of cell dimensions found for Pt(bpy)(CN)₂ with those reported by Che *et al.*⁹

	This work.	Che <i>et al.</i>
Space group	<i>Cmcm</i>	<i>Cm2m</i>
a , Å	18.142(5)	18.154(5)
b , Å	9.361(2)	9.357(2)
c , Å	6.659(1)	3.3296(4)
V , Å ³	1130.9(4)	565.6(2)
Z	4	2
D_{cal} , g cm ⁻³	2.369	2.368*

* Che *et al.*⁹ actually reported D_{cal} =3.368 and D_{measd} =3.39.

The answer is that Che *et al.*⁹ chose to describe the structure in a non-centrosymmetric space group, *Cm2m*. (It was actually cast in a different setting, *C2mm*; both are conventionally described as *Amm2*, no. 38.) In modeling X-ray diffraction data we attempt to minimize - for all reflections (*hkl*) - the difference between the magnitude of the experimentally determined structure factor, $|F_{\text{obs}}|$, and the magnitude of the calculated structure factor, $|F_{\text{cal}}|$. The formula for $|F_{\text{cal}}|$ is:

$$|F_{\text{cal}}| = \sqrt{A_{\text{cal}}^2 + B_{\text{cal}}^2} \quad (3.2)$$

where *A* and *B* are, respectively, the cosine (real) and sine (imaginary) components of the expression for the structure factor. Note that the *B* term is identically zero for a centrosymmetric space group. Therefore, because the structure was described in a non-centrosymmetric space group, an “imaginary,” out-of-phase component - a *B* term when the Pt atom is positioned at *y*=0, as chosen by Che *et al.*⁹ - was introduced into each of the F_{cal} values. This *B* term is almost entirely due to contributions from the lighter atoms and hence is relatively small. Since the Pt atoms lie very close to the origin of the cell, the “real” terms - A_{cal} - are almost invariably large. Accordingly, the relatively small B_{cal} terms have little influence on the resulting values of $|F_{\text{cal}}|$, and thus, the agreement with the observed data. However, these *B* terms can reflect appreciable asymmetry in the apparent arrangement of the lighter atoms; in effect, they resolve the centrosymmetric superposition of the two molecules (Figure 3.3d) into a single, polar molecule.

To confirm this explanation, we have carried out refinements in the space group selected by Che *et al.*,⁹ *Cm2m*, and also in its centrosymmetric analogue, *Cmmm*, based on the sub-cell data containing only *l*-even reflections. Thus, all reflections with *l* odd were deleted from the data set and the *l* values of the remaining reflections were halved. There resulted 1394 reflections for refinement in *Cm2m* (the averaging of intensities was according to point group *m2m*) and 762 for *Cmmm* (point group *mmm*). For completeness, we repeated the *Cm2m* refinement with the sign of *f*'' (the imaginary

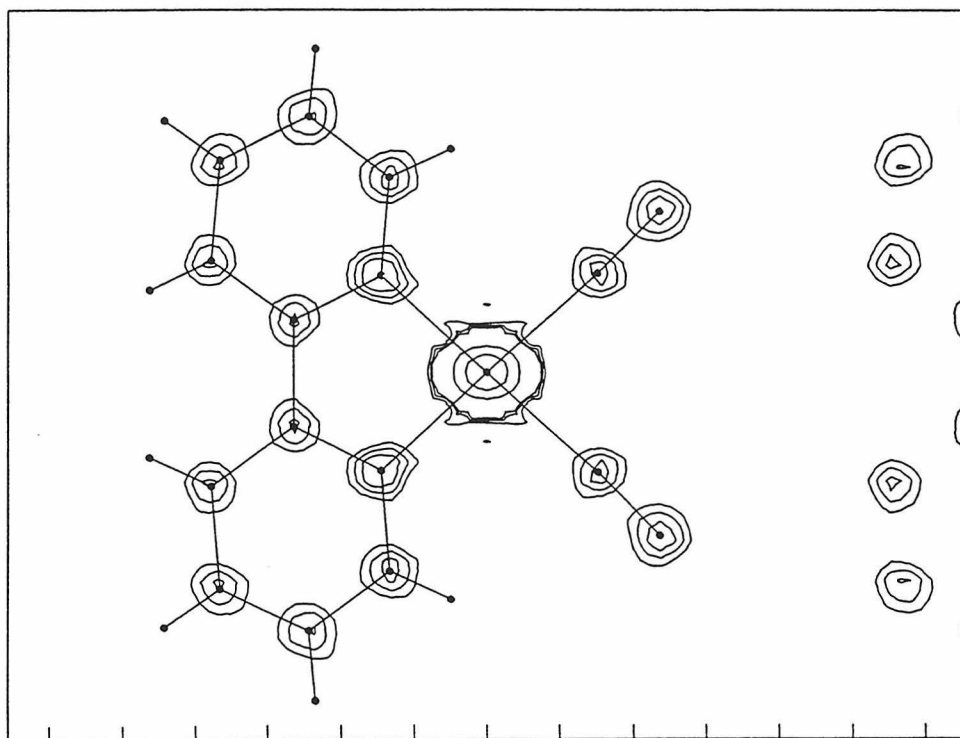
Table 3.8. Selected data from refinements in *Cmcm*, *Cmmm* and *Cm2m*.^a

	<i>Cmcm</i> (no. 63)	<i>Cmmm</i> (no. 65)	<i>Cm2m</i> (no.38)	<i>Cm2m</i> (no.38)
			(enantiomorph A)	(enantiomorph B)
<i>a</i> (Å)			18.142(5)	
<i>b</i> (Å)			9.361(2)	
<i>c</i> (Å)	6.659(1)	3.329(1)	3.329(1)	3.329(1)
Volume (Å ³)	1130.9(4)	565.4(3)	565.4(3)	565.4(3)
No. Reflens	1363	762	1450	1450
No. Reflens $F_o^2 > 0$	1287	741	1394	1394
No. Reflens $F_o^2 > 3\sigma(F_o^2)$	1096	641	1142	1142
No. Parameters	54	47 ^b	47 ^b	47 ^b
GOF	1.56	1.88	1.68	1.71
R	0.0453	0.0444	0.0516	0.0514
$R(F_o^2 > 3\sigma(F_o^2))$	0.0349	0.0359	0.0397	0.0397
Pt U_{eq} (Å ² x 10 ⁴)	274(1)	394(1)	390(1)	390(1)
N1 U_{eq} or U_{iso} (Å ² x 10 ⁴)	337(12)	379(49)	398(38)	360(35)
C5 U_{eq} (Å ² x 10 ⁴)	382(14)	404(23)	391(20)	399(21)
C6 U_{eq} or U_{iso} (Å ² x 10 ⁴)	380(15)	328(47)	318(37)	352(39)
Pt - N1 (Å)	2.059(5)	1.92(2)	2.04(2)	1.96(2)
Pt - C6 (Å)	1.949(7)	2.08(2)	1.95(2)	2.04(2)
N2 - C6 (Å)	1.15(1)	1.15(1)	1.27(2)	1.18(2)
N1 - C5 (Å)	1.363(8)	1.36(2)	1.29(2)	1.34(2)
N1 - Pt - N1' (°) ^a	79.8(2)	88.0(7)	83.9(7)	85.4(7)
C6 - Pt - C6' (°) ^a	88.3(3)	80.5(8)	83.9(7)	81.9(8)
Pt - C6 - N2 (°)	177.7(6)	171.8(17)	178.0(14)	175.0(16)

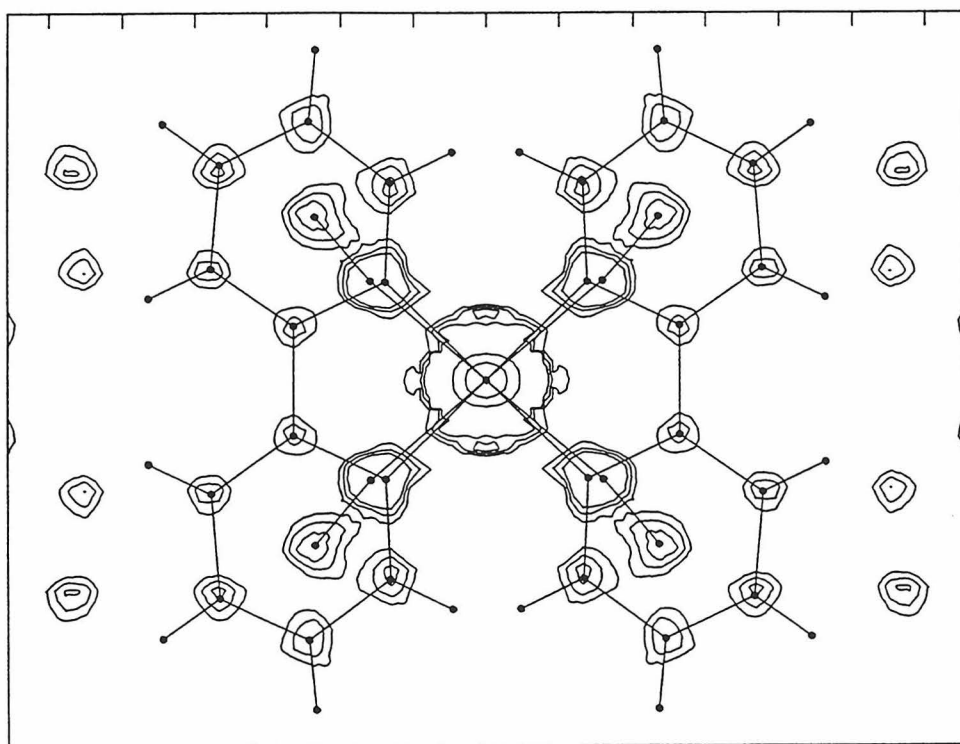
^a Primed atoms are related by a mirror plane: -x, y, z^b Because of the severe correlation between N1 and C6, these atoms were assigned isotropic *B* values.

Figure 3.4 Electron density projection maps along the c axis for the structure described in space groups: (a) $Cm2m$ with contour levels at 4.0, 5.6, 7.2, 50, and $100 \text{ e}\text{\AA}^{-2}$; (b) $Cmmm$ with contour levels at 2.4, 3.2, 4.0, 50, and $100 \text{ e}\text{\AA}^{-2}$ (identical to $Cmcm$, except for a factor of 2).

(a)



(b)



component of anomalous dispersion) reversed although, in principle, this should have no effect on the results. A summary of the results of these refinements is given in Figure 3.3b and Table 3.8, together with the *Cmcm* results (based on the complete data set, as in Table 3.3).

What can be made of these results? First, in terms of the final agreement indices *R* and the goodness-of-fit (GOF), there is not a large disparity between the three space groups for this selection of reflections. (Of course, if the odd-*l* reflections had been included for the *Cm2m* and *Cmmm* models, with F_{cal} 's of 0.0 for all such reflections, the distinction would have been obvious.) Nor is there a clear choice between *Cm2m* and *Cmmm*, the latter showing a slightly better *R* due to the averaging of *hkl* and $h\bar{k}l$ but a slightly worse GOF because of the increased weights. The close similarity of these latter two refinement results clearly demonstrates the small effect of the out-of-phase terms, B_{cal} , and emphasizes the common difficulty of distinguishing between a disordered, centrosymmetric structure and an ordered, non-centrosymmetric one.⁵⁷

As a further illustration of the difference between the models, we show in Figure 3.4 electron density projections of the structure onto the [001] plane, calculated with the $F(hk0)_{\text{obs}}$ values phased according to the final *Cm2m* model (Figure 3.4a) and to the *Cmmm* model (Figure 3.4b). As expected, the *Cm2m* map clearly shows the superposition of two disordered molecules related by the additional mirror plane passing through the Pt center. (This map is identical to the one obtained from the complete, correct model in *Cmcm*, since only the *hk0* reflections are involved.) In contrast, the *Cm2m* map shows no evidence of disorder and only a single molecule in one orientation. Thus, the antisymmetric components of B_{cal} , while not large enough to appreciably affect the magnitudes of F_{cal} , have effectively shifted the entire electron density from one apparent atom site *x*,*-y*,*z* to the other true site *x*,*y*,*z* completely destroying the mirror plane and creating a seemingly reasonable, ordered molecule (Figure 3.4a). Some evidence for the disorder persists in the elongation, along *y*, of the electron density

associated with the platinum atom; however, the elongation is small (due to the near coincidence of the two superposed Pt atoms) and can be accommodated by an increase in the U_{22} term for Pt; see Figure 3.3b.

3. *Structural Implications*

So we have here an example in which not only was the unit cell incorrectly assigned (since the weak, odd-order reflections along c were overlooked), but in addition, the structure was incorrectly presumed to be polar when in fact it is centrosymmetric. What were the effects on the resulting structure? In terms of the *molecular* structure - that is, the shape and the dimensions of an individual molecule - they were only moderately serious: atom connectivity was correct (although, certainly much of that was assumed *a priori*), and bond lengths and angles were not unreasonable. The most serious errors were in the bond lengths involving the Pt atom: Pt-N and Pt-C were previously reported as 2.00(1) Å and 2.01(2) Å, respectively,⁹ whereas we find 2.059(5) and 1.949(7) Å. It is surely no coincidence that these two bonds were found to be essentially equal in the earlier work, since the N and C atoms are almost exactly superposed in the disordered structure that results when the odd layer lines are ignored (the '*Cmmm*' structure discussed earlier; Figure 3.4b).

In terms of the entire crystal structure, however, the earlier results were seriously in error, since alternating molecules were rotated by 180° (or reflected across a mirror plane) relative to their correct positions. Thus, whereas the earlier structure featured an eclipsing of successive molecules with a linear Pt...Pt...Pt chain and, surprisingly, overlap of the ligands, the revised structure shows a slightly zigzag chain and alternating stacking of ligands along the chain. The Pt...Pt distance is slightly increased, from 3.3296(4) in the earlier work to 3.3461(5) Å. This packing arrangement is entirely consistent with the structures of other linear-chain platinum(II) diimine complexes (*vide*

infra). We presume that the palladium analogue, $\text{Pd}(\text{bpy})(\text{CN})_2$, which was reported⁹ to be isostructural with $\text{Pt}(\text{bpy})(\text{CN})_2$, also adopts this stacking geometry.

In these days when the derivation of the unit cell usually depends on an automated diffractometer search for relatively strong reflections, one should be continually concerned that weak layer lines might have been overlooked. In most cases, such weak layer lines evidence a superstructure based on only slight perturbations from an average sub-structure; the sub-structure that results from ignoring weak layer lines may be entirely reasonable except for some enlarged displacement ellipsoids. In the present case (where a heavy atom is involved) the consequences were far more serious. At the very least, diffractometers should be programmed so as to routinely search for significant intensity at intermediate reciprocal lattice points. But a far more sensible procedure would be to routinely prepare diffraction photographs so that the entirety of reciprocal space can be examined for sub-cell reflections; the use of area detectors may also be an effective counter-measure. In the current case and presumably that of the Pd analogue as well, these additional reflections indicate that very important changes to the sub-structure need to be made. This result underscores a recurrent theme in scientific research: while automation and computation have greatly reduced the time and effort involved in producing results, they have not eliminated the need for judgment, care and thought in conducting an experiment.

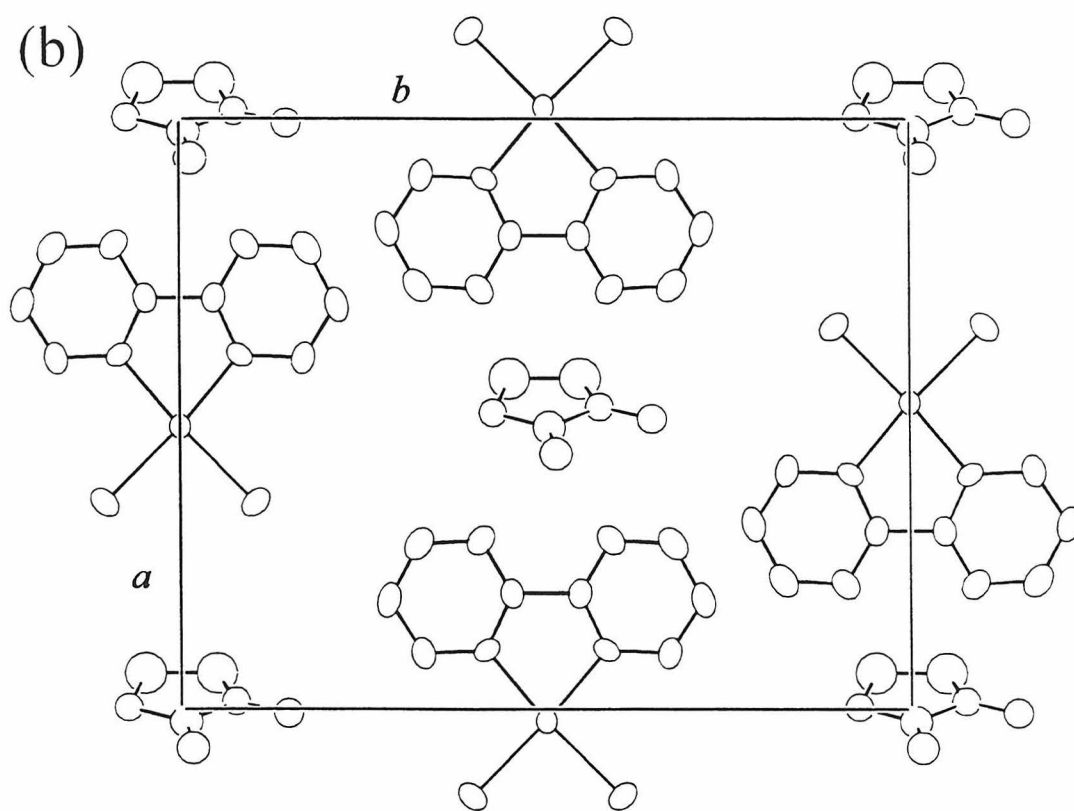
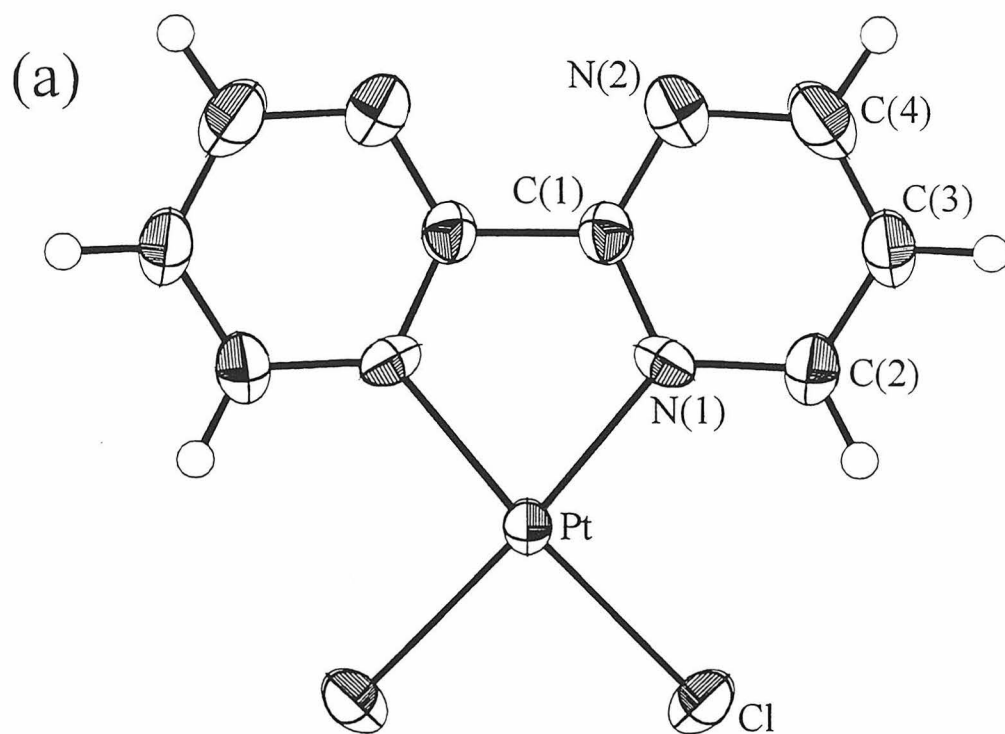
C. Other Linear-Chain Platinum(II) Diimine Complexes

Selected distances and angles for **1b**, **3**, **6**, and **7** are given in Table 3.6. Figure 3.5 shows the platinum complexes and views of their packing.

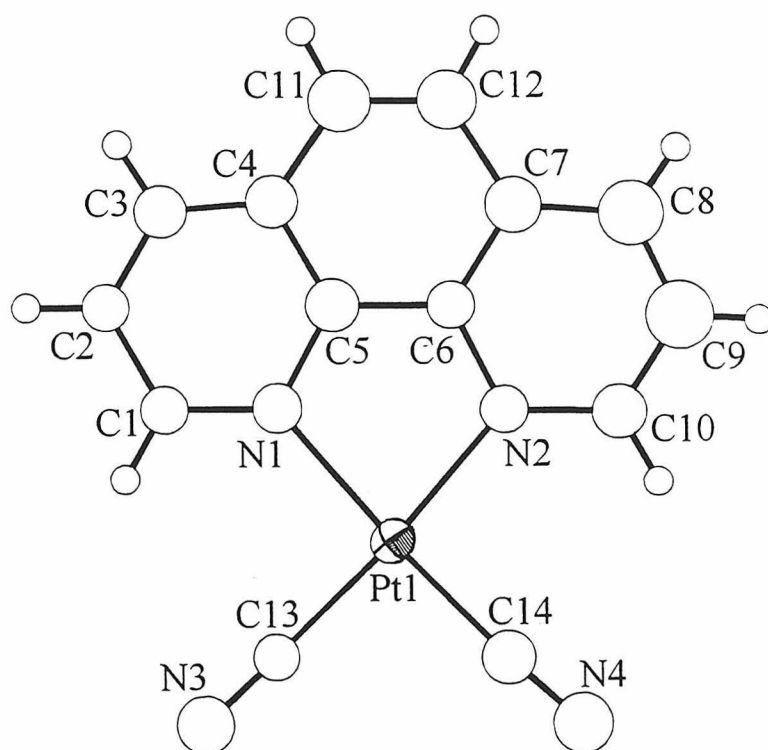
*1. $\text{Pt}(\text{bpm})\text{Cl}_2 \cdot 0.5(\text{nmp})$ (**3**)*

Kiernan and Ludi¹⁶ previously noted that $\text{Pt}(\text{bpm})\text{Cl}_2$ forms both yellow and red solids; the color of the red material is suggestive of a linear-chain structure. The

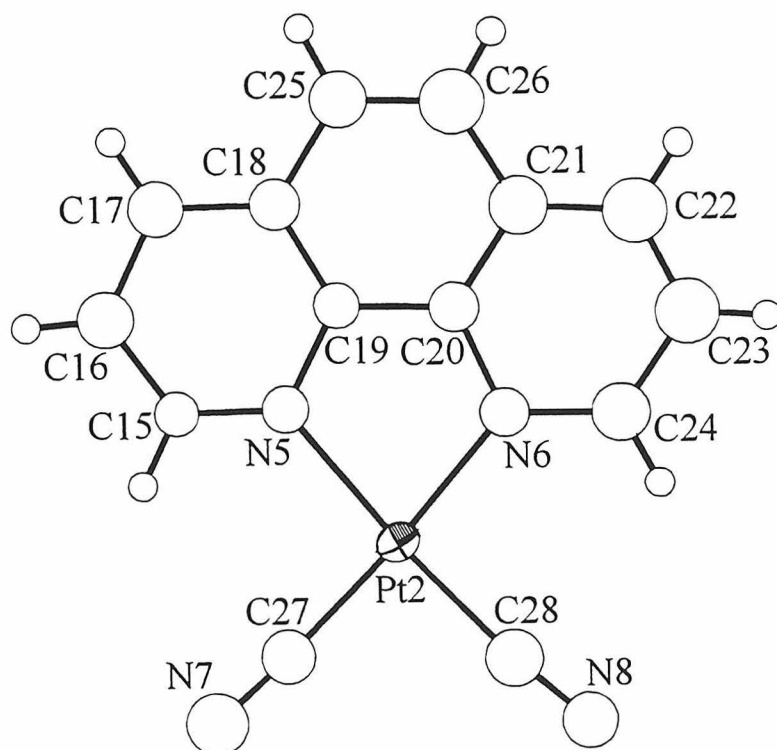
Figure 3.5 Structures of linear-chain platinum(II) diimine complexes and the yellow form of Pt(dmbpy)(NCO)₂. *ORTEP*II²⁹ diagrams with 50% probability ellipsoids showing: (a) Pt(bpm)Cl₂ (**3**); (c,d) both molecules of Pt(phen)(CN)₂ (**6**), (f) Pt(bpy)(NCS)₂ (**7**), and (h) Pt(dmbpy)(NCO)₂ (**1b**). Atoms that were refined isotropically are shown as hollow spheres; H atoms are shown as spheres of arbitrary size. Crystal packing for: (b) **3** (one orientation of solvent is shown and O atom has been given a *B* value of 3.3), (e) **6**, (g) **7**, and (i) **1b**. H atoms are not shown.

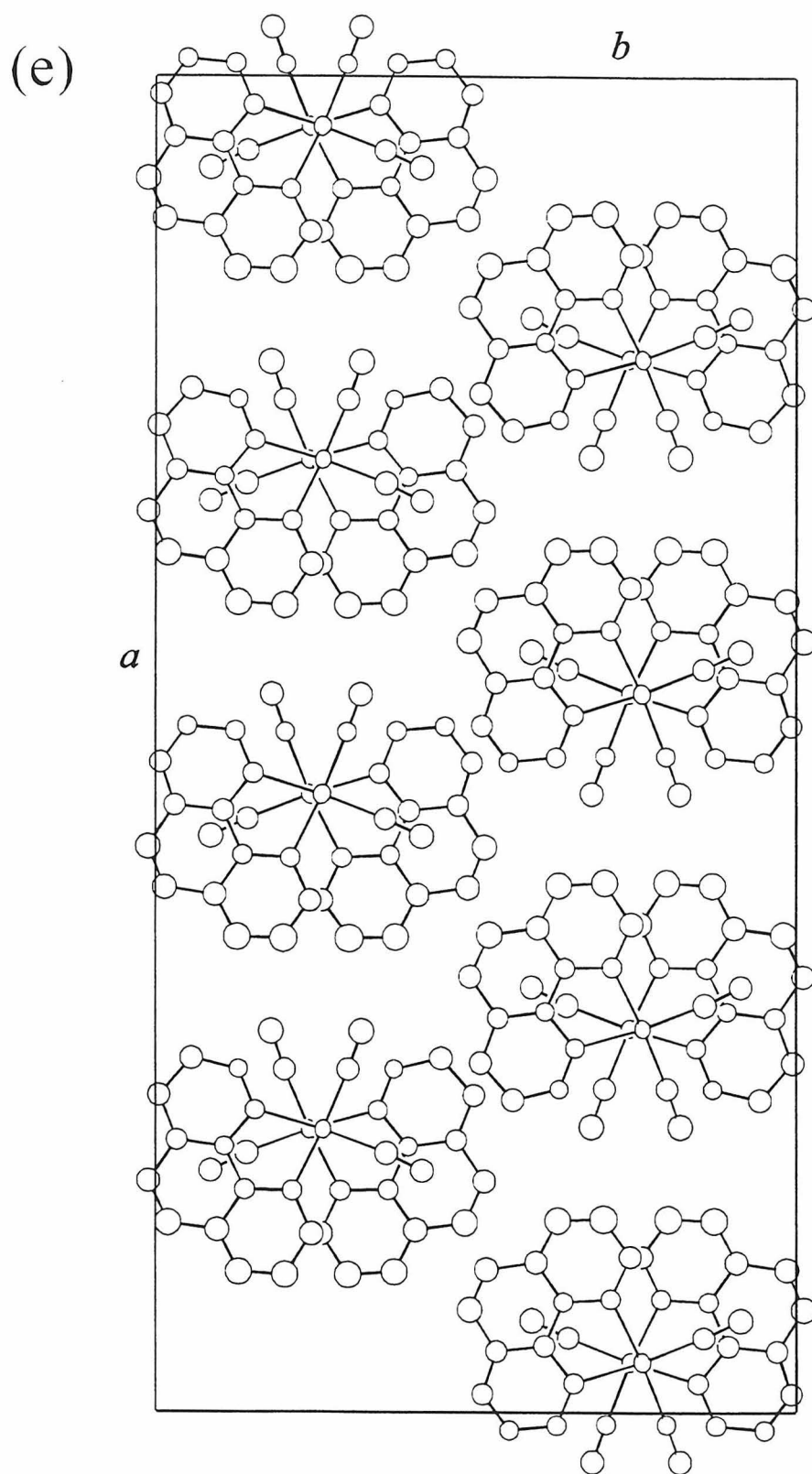


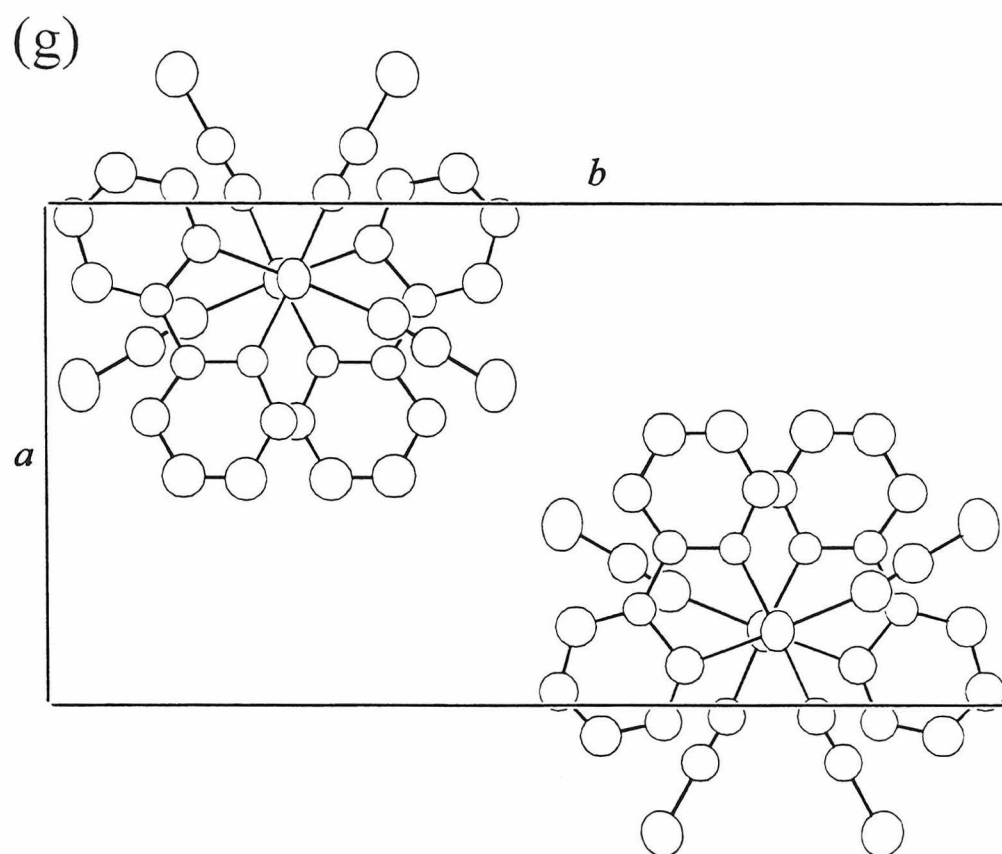
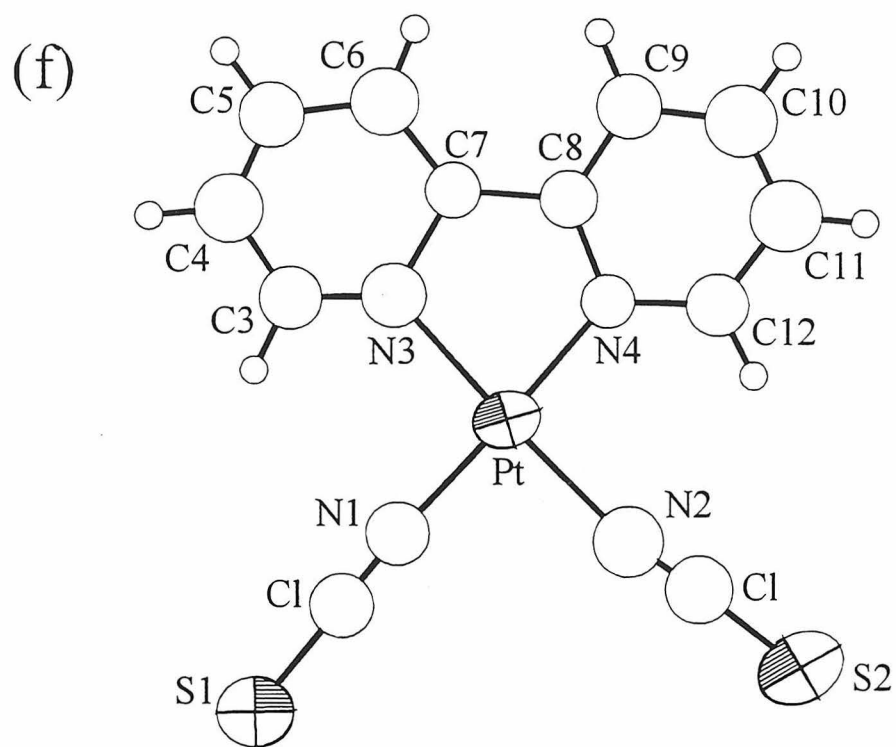
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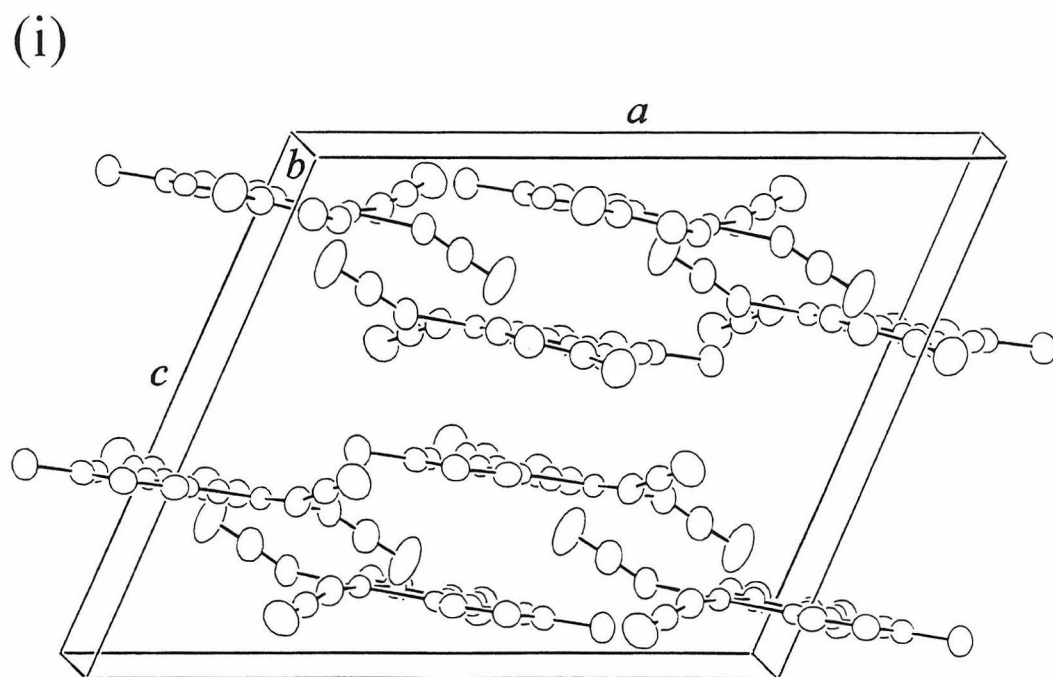
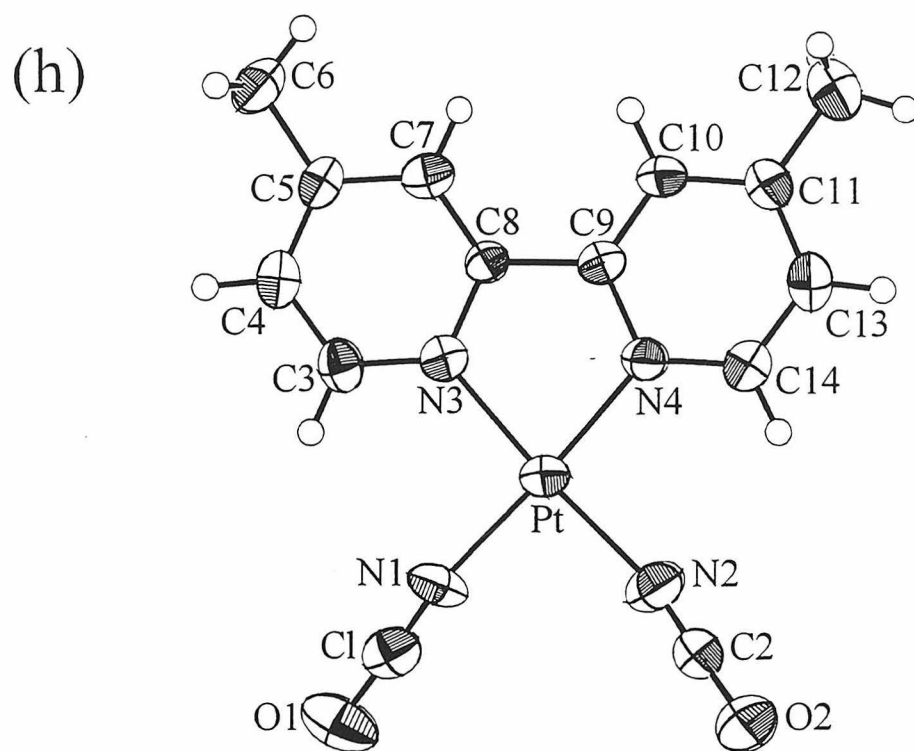


(d)









approximately planar Pt(bpm)Cl₂ units are bisected by a mirror plane ($y = 0$) passing through the Pt atom. Overall, the molecular geometry is similar to that found for Pt(bpy)Cl₂.^{8,38,51,52,58} The Pt-N and Pt-Cl distances (2.006(8), 2.294(3) Å) and the diimine bite and Cl-Pt-Cl angles are nearly identical with the values reported for the red and yellow forms of Pt(bpy)Cl₂ (yellow form: 2.006(10), 2.011(10); 2.281(4), 2.300(3) Å; 80.6(4); 89.1(1)°;^{38,52} red form: 2.009(6); 2.302(2) Å; 80.2(2); 89.1(1)°).⁵⁸ There are no unusually close contacts between the disordered solvent region and the Pt complex.

The complexes stack along the c axis to form a chain of Pt(bpm)Cl₂ units with short interplanar spacings (3.3–3.4 Å); successive molecules are related by an inversion center, and thus appear rotated by 180° in an antiparallel arrangement when viewed along the c axis (Figure 3.5b). This packing leaves channels between the chains that are occupied by solvent. The mean plane defined by the Pt and coordinated N and Cl atoms is nearly perpendicular to the stacking axis; the angle is 86.1(1)°. The Pt atoms are offset from the chain axis by 0.257(1) Å along a , but lie very close to $z = 1/4$ and $3/4$; the two Pt...Pt distances (3.371(1), 3.411(1) Å) along the chain are nearly equal with a Pt...Pt...Pt angle of 162.55(2)°. The distances are slightly shorter than that found for stacked Pt(bpy)Cl₂ complexes (3.449(1) Å; Pt...Pt...Pt, 161.03(3)°).^{8,58}

2. Pt(*phen*)(CN)₂ (**6**)

The violet color of this material⁹ prompted our structural investigation. Two Pt(*phen*)(CN)₂ molecules, approximately related by a translation of 1/4 along a , form the asymmetric unit (Figure 3.5cd). During refinement, this pseudo-symmetry caused high correlation between the parameters describing the two molecules, and consequently the resulting distances and angles are imprecise. Taking into account the largest covariance terms, the e.s.d. of the difference (0.09 Å) between the Pt1-N2 and Pt2-N6 bond lengths is 0.03 Å; the e.s.d. of the difference (0.06 Å) between the Pt1-C13 and Pt2-C27 bond lengths is 0.06 Å.

The Pt1 and Pt2 complexes stack separately along *c* to form two types of chains; because of the pseudo-symmetry, the differences between the Pt1 and Pt2 chains are subtle. When viewed down *c*, successive units appear rotated by approximately 133° (Figure 3.5e); the mean plane defined by the Pt and coordinated atoms (C, N) forms an approximately 84° angle with the stacking axis. Because Pt1 and Pt2 are offset by different amounts from the chain axes (0.172(2), 0.198(2) Å), the Pt...Pt distances (3.332(1), 3.338(1) Å) and the Pt...Pt...Pt angles (168.07(4), 166.30(4)°) are slightly different for the two chains.

3. *Pt(bpy)(NCS)₂* (7)

In the solid state, the dithiocyanato complex of Pt(bpy) is known to occur in (at least) two isomeric forms, with identical stoichiometry, but distinctly different chemistry and spectroscopy. Yellow S-bonded Pt(bpy)(SCN)₂ is soluble in coordinating solvents and readily converts to the less-soluble N-bonded red form.^{22,59,60} These observations led to our investigation of the structure of the red form (7), whose color is suggestive of Pt...Pt interactions. (We have been unable to prepare crystals of the S-bonded yellow form, apparently as a result of its tendency to convert to the red form.) The neutral Pt(bpy)(NCS)₂ units lie on mirror planes at *z*=1/4 and 3/4; the coordination geometry of the Pt is approximately square planar. The crystal diffracted poorly and the coordinates of the lighter atoms (C and N) are not well-determined. Nevertheless, it is clear that the thiocyanate ligands are nearly linearly coordinated to the Pt with Pt-N-C(thiocyanate) angles of 176.6(8) and 177.4(9)°, characteristic of an N-bonded conformation.

The complexes stack along the *c* axis to form a chain of Pt(bpy)(NCS)₂ units with a relatively short interplanar distance of 3.286(2) Å (= *c*/2); consecutive molecules are related by the *c*-glide perpendicular to *b*. When viewed down the stacking axis (*c*), successive molecules along this chain are rotated by approximately 137°; this staggered arrangement places the bulky S atoms on the periphery of the column of molecules

(Figure 3.5g). The Pt atoms are displaced by 0.143(2) Å (along *b*) from the chain axis, resulting in a Pt...Pt distance of 3.299(2) and a Pt...Pt...Pt angle of 170.04(5)°.

Interestingly, a previous EXAFS (extended X-ray absorption fine structure) study of this material at 15 K suggested two short intermolecular Pt...Pt distances (3.24 ± 0.05 and 4.52 ± 0.02 Å).^{22,61} The shorter distance is entirely consistent with our room-temperature structure; spectroscopic studies of **7** indicate a substantial contraction of the Pt...Pt separation at low temperature (Chapter 4), as often observed for Pt(II) linear chains.^{6,58} The longer distance obtained from the EXAFS experiment is more difficult to explain, since the next shortest Pt...Pt distance in the crystal is 6.572(3) Å (= *c*). One explanation is that the observed peak in the radial distribution function corresponds to the *intramolecular* Pt...S distance (4.70(1), 4.72(1) Å). However, the possibility of a phase transition cannot be ruled out.

4. *Pt(dmbpy)(NCO)₂* (**1b**)

Slow evaporation of an nmp solution of Pt(dmbpy)(NCO)₂ gives both orange (**1**) and yellow (**1b**) crystals. The unit-cell determined for a single orange crystal (*a*, 18.672(8); *b*, 11.878(5); *c*, 6.671(5) Å; $\alpha = \beta = \gamma = 90^\circ$) is in reasonable agreement with that previously reported for the linear-chain structure (*a*, 18.722(6) Å; *b*, 11.889(5); *c*, 6.688(5) Å; $\alpha = \beta = \gamma = 90^\circ$).¹² In contrast, the yellow crystals (**1b**) contain Pt(dmbpy)(NCO)₂ units with intermolecular contacts at van der Waals distances or greater; the shortest Pt...Pt distance is 4.957(1) Å. The molecular geometry is in excellent agreement with those reported for the orange form (**1**)¹³ and the unmethylated analogue, Pt(bpy)(NCO)₂ (**9**):¹⁰ The Pt-N-C bond angles (160.2(6) and 153.9(6)°) are significantly less than 180°, but similar to the value reported for the orange isomer (159.1(16)°).¹³ A consequence of the bent cyanate coordination geometry is a substantial displacement of the C and O cyanate atoms from the Pt coordination plane (defined by Pt, N1, N2, N3, and N4): C1, -0.39; C2, 0.49; O1, -0.73; O2, 0.94 Å; in

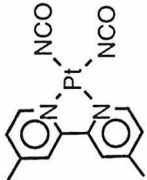
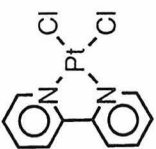
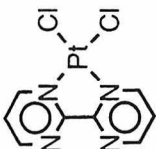
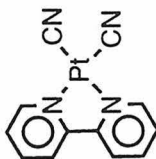
contrast, the cyanate ligands lie in the coordination plane by symmetry in the linear-chain form (**1**). The planar Pt-bipyridyl units interleave to form a columnar structure with spacings between Pt coordination planes of 3.4-3.5 Å (Figures 5i, 8a); this packing arrangement is 7% denser than that found in the orange form (**1**).¹⁰

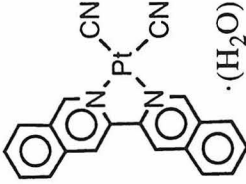
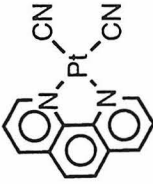
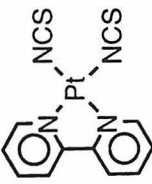
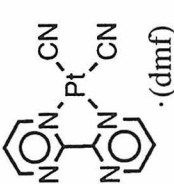
D. Structural Trends

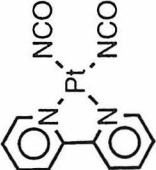
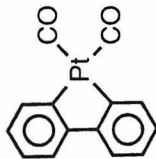
Room-temperature structural data for linear-chain platinum(II) diimine complexes (**1-9**)^{11,13,14,22,40,58} are summarized in Table 3.9. (The closely related compound **10**, Pt(bph)(CO)₂ (bph = biphenyl dianion),⁶² also is included.) Each of the compounds **1-9** is intensely colored in the solid state. This color is due to an electronic transition to the ¹MLCT[dσ*(Pt)→π*(diimine)] state, where the LUMO (π*) is predominantly centered on the diimine ligand (see Chapter 4). With decreasing Pt···Pt distance, enhanced 5d_{z2}···5d_{z2} interaction causes a red-shift in this transition, and the color changes from orange to blue.⁶³ This electronic structural model also is consistent with the yellow colors of the polymorphs of Pt(bpy)Cl₂ and Pt(dmbpy)(NCO)₂, because their shortest Pt···Pt contacts are greater than 4.4 Å.

The packing in these materials is in accord with the principle that free volume in crystals is energetically unfavorable.^{64,65} The columnar structure constitutes an efficient packing motif; in fact, related compounds such as Pt(bpy)I₂,⁴³ and the yellow polymorphs of **1**, **2**, and **8** (*vide infra*), which have longer Pt···Pt contacts than their chain counterparts, also adopt columnar structures. In addition, the stacked complexes tend to avoid like-like interactions (Figure 3.6); when viewed down the chain axis, successive molecules are rotated by an angle, φ, ranging from 120 to 180° (Table 3.9). Interestingly, space group *Cmcm* (no. 63) is disproportionately represented with five of the compounds packing according to this symmetry;⁶⁶ the *mm2* site symmetry of the Pt complex in these structures readily accommodates the C_{2v} molecular symmetry, while the *c*-glide plane relating successive stacked complexes results in a φ of 180°. Thus, for

Table 3.9. Structural Properties of Linear-Chain Platinum(II) Diimine Complexes.

	Compound (color)	Pt...Pt (Å)	Interplanar Spacing (Å)	Pt...Pt...Pt (°)	Tilt Angle ^a (°)	Chain Torsion, ^b φ (°)	Pt- N(diimine)	Reference
	[Space group]						(Å)	
	Pt(dmbpy)(NCO) ₂ (orange)	3.493(3)	3.443(3)	146.30(4)	90	180	2.01(1)	12
	[<i>Cmcm</i> , no. 63]							
	Pt(bpy)Cl ₂ (red)	3.448(1)	3.402(1)	161.03(3)	90	180	2.009(6)	(d)
	[<i>Cmcm</i> , no. 63]							
	Pt(bpm)Cl ₂ ·0.5(nmp) (red)	3.411(1)	3.330(1)	162.55(2)	86.1(1)	180	2.006(8)	(d)
	[<i>C2/m</i> , no. 12]	3.371(1)	3.358(1)					
	Pt(bpy)(CN) ₂ (red)	3.346(1)	3.330(1)	169.6(1)	90	180	2.061(5)	(d)
	[<i>Cmcm</i> , no. 63]							

5		Pt(<i>i</i> -biq)(CN) ₂ (orange-red) [<i>Pbcm</i> , no. 57]	3.342(2)	3.341(2)	177.2	90	147	2.03(1) 2.07(1)	14
6		Pt(phen)(CN) ₂ (violet) [<i>Pbca</i> , no. 61]	3.338(1)	3.31 ^c	166.30(4)	83.7(7)	133	2.08(2) 2.06(2) 2.04(2) 1.99(2)	(d)
7		Pt(bpy)(NCS) ₂ (red) [<i>Pbcm</i> , no. 57]	3.299(2)	3.286(2)	170.04(4)	90	137	2.06(2) 1.91(2)	(d)
8		Pt(bpm)(CN) ₂ ·(dmf) (red) [<i>Cmcm</i> , no. 63]	3.284(1)	3.259(1)	165.9	90	180	2.042(8) 2.057(7)	11

9 	Pt(bpy)(NCO) ₂ (blue) [P3 ₁ 2I, no. 152]	3.235(2)	3.229(2) ^c	174.1	87.9	120	1.99(2)	10
10 	Pt(bph)(CO) ₂ (green) [Cmcm, no. 63]	3.2426(3)	3.2030(3)	162.1	90	180	—	62

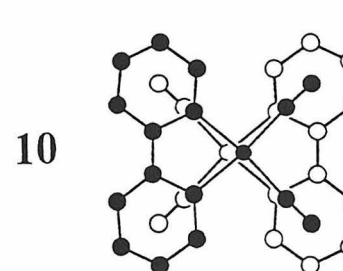
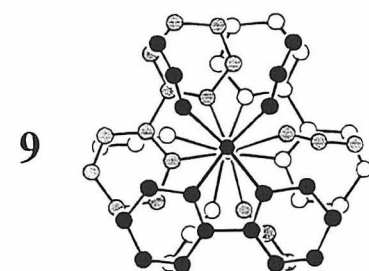
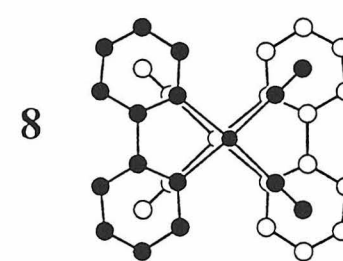
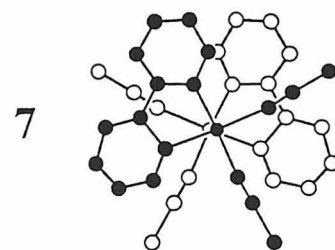
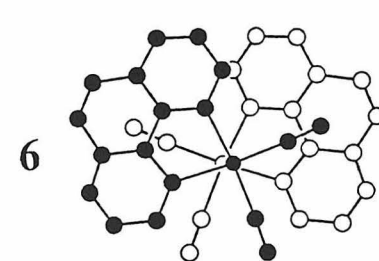
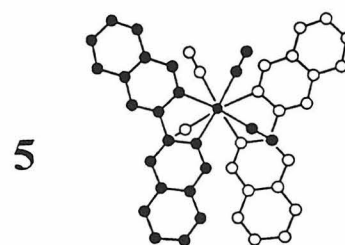
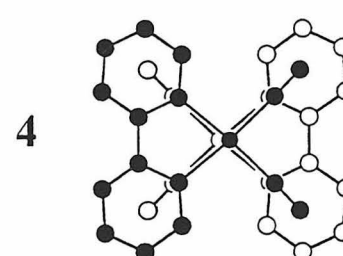
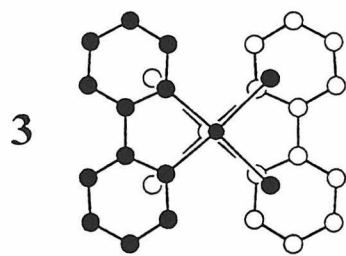
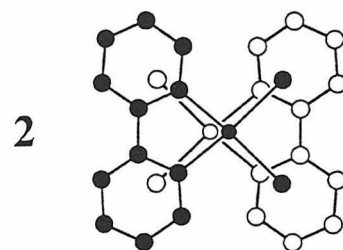
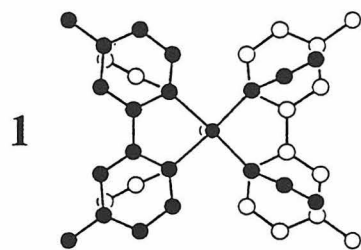
^a The angle between the chain axis and the mean plane defined by the Pt and the four coordinated atoms.

^b The angle of rotation of successive stacked complexes when viewed down the chain axis.

^c Average interplanar spacing.

^d This work.

Figure 3.6 Stacking motifs of platinum(II) diimine complexes; one repeat unit of chains **1-10**, viewed in projection along the stacking axis. H atoms are not shown.



compounds **1**, **2**, **4**, **8**, and **10** (as well as **3**, which crystallizes in $C2/m$), the halide or pseudohalide ligands are sandwiched between the pyridyl rings of the diimine ligands of adjacent stacked complexes (Figure 3.6). In analogy to Miller's description of interactions in partially oxidized Pt(oxalato) chain structures,⁶⁷ this antiparallel arrangement can accommodate weak intermolecular bonding between the occupied orbitals of the anionic ligands and the π^* orbital of the diimine ligand of an adjacent complex.

Aside from the short metal-metal contacts, several other observations point to the importance of Pt...Pt interactions in determining the structures of these materials. Both the near linearity of the Pt chains and the proximity of the tilt angles (the angle between the chain axis and the mean plane defined by the Pt and the four coordinated atoms) to 90° suggests a tendency to form short Pt...Pt contacts while minimizing steric repulsions between other atoms. In addition, though the interplanar spacings of several of the compounds in Table 3.9 are within the range of π - π stacking contacts, the diimine ligands of successive complexes are rotated away from one another. Also, when solvent is present (**3**, **5**, **8**), the solvent molecules are relegated to channels parallel to the Pt chains; these sites are disordered or partially occupied, suggesting the absence of strong specific interactions with the metal complexes. Furthermore, the Pt...Pt distances in these complexes exhibit a characteristically strong temperature dependence. As discussed earlier, cooling of **2** from room temperature to 20 K results in a $0.080(2)$ Å decrease in the Pt...Pt distance;⁵⁸ similarly, at 160 K the Pt...Pt distance in **8** is shortened by $0.024(2)$ Å from the room-temperature value.⁶⁸

Interestingly, there is no definitive evidence of the Pt...Pt interaction perturbing the molecular dimensions. However, the intramolecular electronic effects do impact on the molecular geometry. For instance, complexes with cyanide ligands generally have longer *trans* Pt-N bonds than the other complexes (*e.g.*, Pt(bpy)(CN)₂ (**4**), $2.061(5)$;

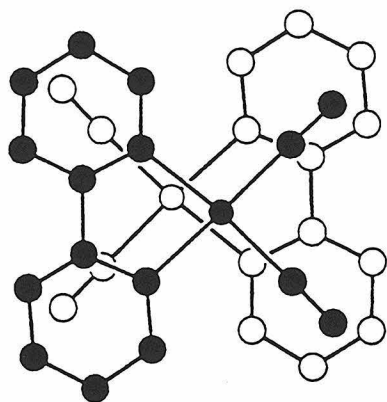
Pt(bpy)Cl₂ (**2**), 2.009(6) Å). This effect is a consequence of the strong σ -donor/ π -acceptor character of the cyanide ligand.

E. Polymorphism

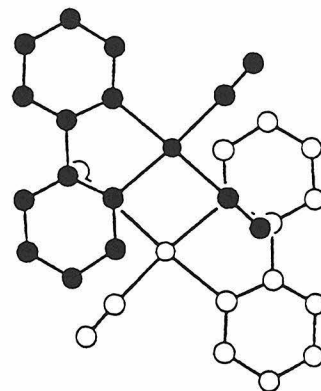
Platinum(II) diimine complexes that form linear-chain structures often exist in other crystal forms as well, indicating that the Pt $\cdots$ Pt bonding may be offset by other favorable interactions.⁶⁹ For example, **4** crystallizes as a yellow hydrate, and **8** forms both yellow hydrated⁷⁰ and yellow unsolvated solids.⁷¹ Also, as mentioned earlier, the yellow form of **7** is an S-bonded solid;^{22,60} most likely, the bent thiocyanato coordination geometry⁷² disfavors stacking. Furthermore, there is considerable spectroscopic evidence for monomer/chain polymorphism in several other compounds that remain structurally uncharacterized.⁷³

The polymorphs of **8**^{11,70,71} illustrate the interplay of subtle intermolecular forces in stabilizing these columnar structures. The hydrated form, Pt(bpm)(CN)₂·H₂O,⁷⁰ consists of a chain of dimers (Pt $\cdots$ Pt = 3.44, 4.32 Å) with spacings between the molecular planes (defined by the Pt and coordinated N and C atoms) of 3.29 (intradimer) and 3.32 Å (interdimer) (Figure 3.7ab). The molecules comprising the dimer adopt an antiparallel arrangement as found for the linear-chain form; the cyanide groups lie in close proximity to the bpm ligands of an adjacent molecule with a shortest C(cyanide) $\cdots$ C(bpm) contact of 3.39 Å (Figure 3.7a). Also, there are very close contacts between the cyanide and bpm groups *between* dimers (*e.g.*, C(cyanide) $\cdots$ N(bpm), 3.31; N(cyanide) $\cdots$ C(bpm), 3.23 Å), once again indicating the presence of interligand bonding (Figure 3.7b). In the linear-chain structure (**8**),¹¹ the shortest C(cyanide) $\cdots$ N(bpm) distance is 3.27 Å (Figure 3.6). Similarly, the unsolvated form consists of two chains of dimers, α (Pt $\cdots$ Pt = 3.44, 4.18 Å) and β (Pt $\cdots$ Pt = 3.27, 4.58 Å).⁷¹ Interplanar spacings in the α chain are 3.26 (intradimer) and 3.25 Å (interdimer), and the stacked molecules adopt orientations remarkably similar

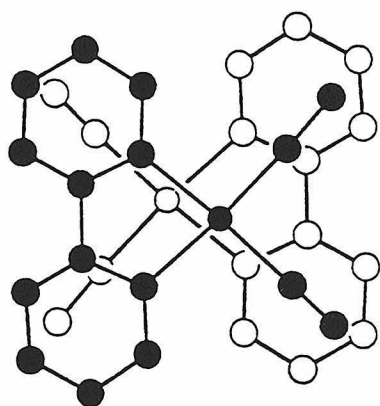
Figure 3.7 Intermolecular interactions in polymorphs of $\text{Pt}(\text{bpm})(\text{CN})_2$. View in projection along the stacking axis (perpendicular to molecular planes) showing (a) intradimer and (b) interdimer interactions in $\text{Pt}(\text{bpm})(\text{CN})_2 \cdot \text{H}_2\text{O}$,⁷⁰ as well as (c,e) intradimer and (d,f) interdimer interactions in the α and β chains of $\text{Pt}(\text{bpm})(\text{CN})_2$.⁷¹



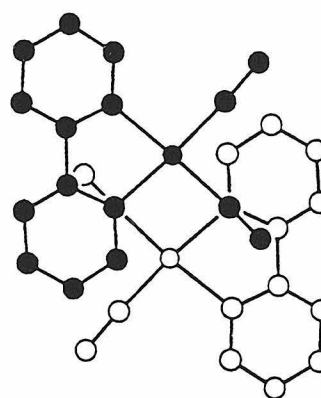
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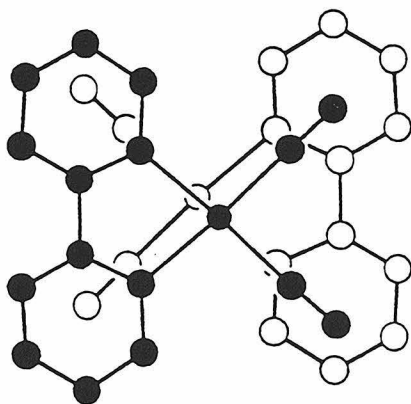
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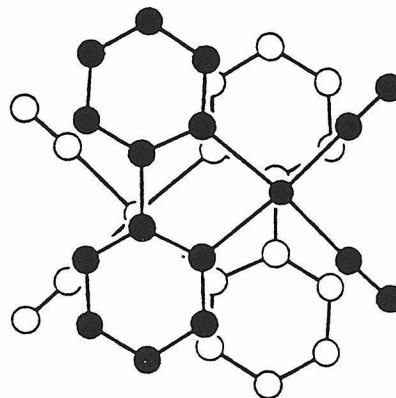
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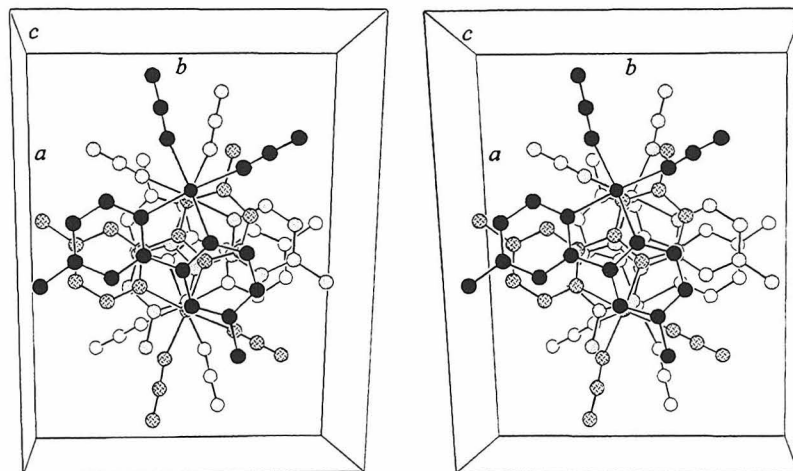
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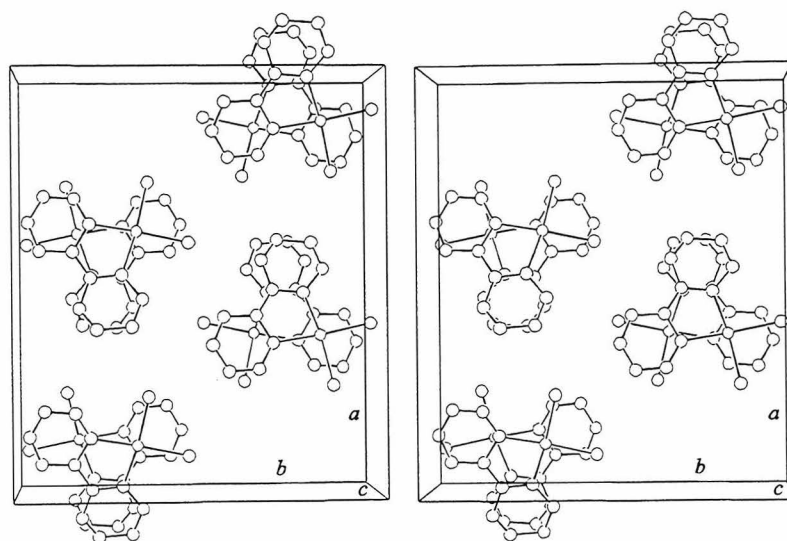
(f)

Figure 3.8 Stereoviews of crystal packing: (a) the yellow form of $\text{Pt}(\text{dmbpy})(\text{NCO})_2$ (**1b**) with four of the molecules in the unit cell shown; and (b) the yellow form of $\text{Pt}(\text{bpy})\text{Cl}_2$.⁵² H atoms are omitted for clarity.

(a)



(b)



to those of the hydrated form (Figure 3.7abcd). In contrast, interplanar spacings in the β chain are 3.27 and 3.49 Å, and the molecules comprising the dimer have nearly the same relative orientation (Figure 3.7ef) as found for the linear-chain structure of **8** (Figure 3.6); the interplanar spacing in **8** is 3.26 Å with a Pt...Pt distance of 3.28 Å. Within a dimer, the shortest C(cyanide)...N(bpm) contact is 3.27 Å; however, the shortest contact between dimers is 3.47 Å (Figure 4f). Thus, we find both Pt...Pt and interligand interactions in all three forms of Pt(bpm)(CN)₂.

The structurally characterized forms of **1** and **2** are especially interesting, since they do not involve changes in crystal composition or ligand isomerism; in both **1b** and the yellow form of Pt(bpy)Cl₂,^{38,52} the Pt atoms are well separated (> 4.4 Å). In the case of **1b**, the complexes stack to form a columnar structure with interplanar spacings of 3.44(2) and 3.46(2) Å. The planar Pt-bipyridyl units efficiently interleave to form the core of the column, whereas bending of the cyanate ligands out of the coordination plane accommodates packing of these and the methyl groups on the periphery of the column (Figure 3.8a). Similarly, the planar Pt(bpy)Cl₂ complexes in the yellow form of **2** stack in a columnar structure with an interplanar distance of 3.722(2) Å (= $c/2$);⁵² the relatively bulky Cl atoms are relegated to the periphery of the column (Figure 3.8b). It is intriguing that the yellow forms of **1** and **2** are, respectively, 7 and 2% *denser* than the linear-chain forms; these relative densities indicate that the linear-chain forms are *less* closely packed, consistent with our expectation that directed intermolecular interactions will give rise to lower density polymorphs. Evidently, the energy costs associated with an increase in free volume are offset by the Pt...Pt bonding interactions in the linear-chain structures.

IV. Conclusions *Factors Governing Stacking*

We have identified three important factors governing the stacking in this series of compounds: interligand steric repulsions, interligand charge-transfer bonding, and Pt...Pt

bonding. Steric effects are suggested by the tendency of successive stacked complexes to avoid eclipsed arrangements. In addition, in the case of **1** the methyl groups account for the 0.26 Å increase in metal-metal distance with respect to **9**; again, these bulky groups are relegated to the periphery of the column of stacked molecules (Figure 3.6).⁷⁴ Also, it must be noted that for the series of compounds **1-10**, complexes with chloride ligands tend to have the longest metal-metal contacts, though this observation also is consistent with electronic effects (*vide infra*). Interligand charge-transfer interactions are indicated by the antiparallel stacking motif in which the halide or pseudohalide ligands are sandwiched between neutral diimine ligands of adjacent molecules in the chain (Figure 3.6). From spatial overlap considerations, these interactions are expected to be weaker than those between the Pt centers. In point of fact, this type of stacking is not found in **5**, **6**, **7**, and **9**, all of which have relatively short Pt...Pt contacts. Thus, the accumulated evidence indicates that the Pt...Pt interactions are the dominant force supporting stacking.

Ligand-field strength has a primary effect on the Pt...Pt bonding, since strong-field ligands destabilize $5d_{z^2}$, enhancing the interactions of stacked complexes. The π -donor/acceptor character of the ligands has a secondary influence; π -acceptor groups decrease electron density on the metal center, thereby reducing electronic repulsions between Pt centers and favoring shorter Pt...Pt distances. Indeed, this description accounts for many empirical trends of linear-chain d^8 systems.^{67,75} In the case of compounds **1-9**, the diimine ligands are good π -acceptors, and thus these molecules are well suited to form chain structures.

The Pt...Pt distances in **1-9** are in general consistent with these electronic considerations. In Table 3.9, there are apparent clusterings of compounds with long, medium, and short metal-metal contacts. Coordination of weak-field π -donor chloride ligands results in longer Pt...Pt distances (**2**, **3**), whereas complexes with the stronger-field N-donor ligands generally have the shortest distances (**7**, **9**). The cyanide

derivatives (**4**, **5**, **6**, **8**) fall in an intermediate range.⁷⁶ The relatively long metal-metal distances in the chloride derivatives are evidently characteristic of the PtN_2Cl_2 system (Table 3.10). For example, *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ complexes stack with metal distances of 3.37 and 3.41 Å;⁷⁷ in the orthorhombic form of $\text{Pt}(\text{en})\text{Cl}_2$ (en = ethylenediamine), the Pt...Pt distance is 3.381(2) Å (*c.f.*, **2** and **3**).⁷⁸ Decreased ligand-field strength also accounts for the slightly longer separation of 3.50 Å in $\text{Pt}(\text{en})\text{Br}_2$,⁷⁹ as well as the 3.673(2) and 3.707(2) Å distances in $\text{Pt}(1,2\text{-benzoquinonedioxime})\text{I}_2$.⁸⁰ While the spacings in this series are also consistent with steric effects, it should be noted that the steric congestion around $\text{Pt}(\text{dada})\text{Cl}_2$ (dada = diaminodideoxyalditol) does not preclude stacking (Pt...Pt = 3.388(2) Å).⁸¹

Table 3.10. Structural Properties of Linear-Chain Platinum Halides.

Compound	Pt...Pt (Å)	Reference
$[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$	3.24	7
<i>cis</i> - $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$	3.37, 3.41	77
$\text{Pt}(\text{en})\text{Cl}_2$, orthorhombic form	3.38	78
$\text{Pt}(\text{en})\text{Cl}_2$, triclinic form	3.42, 3.51	(b)
$\text{Pt}(\text{dada})\text{Cl}_2$, polymorph I ^a	3.39	81
$\text{Pt}(\text{dada})\text{Cl}_2$, polymorph II ^a	3.65	81
$\text{Pt}(\text{en})\text{Br}_2$	3.50	79
$\text{Pt}(\text{amp})(\text{CO})\text{I}^{\text{a}}$	3.50	(c)
$\text{Pt}(1,2\text{-benzoquinonedioxime})\text{I}_2$	3.67, 3.71	80

^a amp = (2-aminomethyl)phenylate; dada = diaminodideoxyalditol.

^b Ellis, L. T.; Hambley, T. W. *Acta Crystallogr.* **1994**, C50, 1888.

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The most compelling evidence for these electronic effects comes from comparison of the bpy complexes with their bpm analogues. These ligands have nearly the same shape and their packing requirements should be very similar. However, their electronic properties are substantially different, because bpm is both a better π -acceptor and a better σ -donor than bpy.⁸² These differences are evident in the structures of compounds **2** and **3**, as well as those of **6** and **8**. The two Pt...Pt distances in Pt(bpm)Cl₂·0.5(nmp) (**3**) are 0.04 and 0.08 Å shorter than in Pt(bpy)Cl₂ (**2**); similarly, the Pt...Pt distance in Pt(bpm)(CN)₂·(dmf) (**8**)¹¹ is 0.06 Å shorter than in Pt(bpy)(CN)₂ (**6**) and 0.05 - 0.06 Å shorter than in the other dicyano structures (**5**, **6**). This observation is consistent with ligand-induced enhancement of the Pt...Pt interactions between stacked complexes.⁸³ The molecular shape of Pt(bph)(CO)₂ (**10**) also is quite similar to that of compounds **6** and **8**; **10** has the shortest Pt...Pt distance of these three compounds, which is entirely consistent with the strong σ -donor properties of the bph ligand and the π -acceptor character of the carbonyl groups.

V. References and Notes

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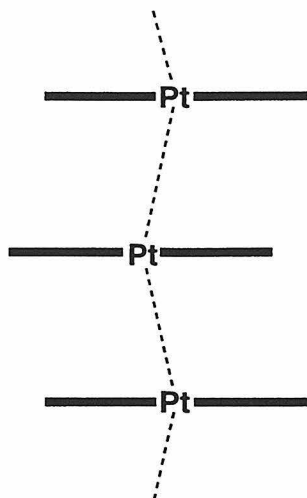
- (76) We have noticed a greater tendency for Pt diimine cyanides to stack than other complexes; this trend is in accord with the strong σ -donor/ π -acceptor character of the cyanide ligand. However, given these electronic considerations, it is intriguing that the cyanide derivatives (**4**, **5**, **6**, **8**) do not stack with shorter Pt...Pt distances than thiocyanate or cyanate analogues (**7**, **9**). It is unlikely that the steric demands of thiocyanate and cyanate are less than those of cyanide. Moreover, several linear-chain $\text{Pt}(\text{CN})_4^{2-}$ salts crystallize with very short metal-metal separations ($< 3.2 \text{ \AA}$) (ref. 4; Krogmann, K.; Stephan, D. *Z. Anorg. Allg. Chem.* **1968**, *362*, 290). One explanation is that the antiparallel stacking motif of **6** and **8**, which favors interligand binding, is incompatible with the very short metal-metal separation favored by the electronic interaction of the Pt centers: thus, derivatives **5** and **6**, which do not adopt an antiparallel arrangement, favor longer separations because of the steric demands of their larger diimine ligands.
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Chapter 4

Spectroscopy of Linear-Chain Platinum(II) Diimine Complexes

I. Introduction

Square planar platinum(II) complexes often form deeply colored linear-chain materials that exhibit intense emission. The planar molecules in these structures stack with short Pt...Pt contacts ($< 3.5 \text{ \AA}$), and the Pt...Pt...Pt chain is sometimes slightly zigzag:¹



Investigations of the spectroscopy of these materials have demonstrated that the maxima of the lowest-energy absorption and emission bands display a strong dependence on the intrachain metal-metal separation.² A dramatic example is Pt(bpy)Cl₂ (bpy = 2,2'-bipyridine), which forms both yellow and red crystalline solids.³ The Pt atoms are well separated in the yellow form ($4.44 \text{ \AA}$);⁴⁻⁶ but in the red form, which is intensely luminescent ($\sim 613 \text{ nm}$) even at room temperature,⁷⁻⁹ the square planar complexes stack to form an approximately linear Pt...Pt chain with a spacing of $3.45 \text{ \AA}$.¹⁰

Recently, linear-chain platinum(II) diimine complexes have attracted interest, in part, because certain water insoluble platinum(II) salts containing bipyridyl ligands (*e.g.*, [Pt(bpy)₂][Pt(CN)₄]) have been shown to undergo photoinitiated ($\lambda > 400 \text{ nm}$) multielectron transfer, sensitizing production of hydrogen from water.^{11,12} Studies of the spectroscopic and photophysical properties of these and related materials have established that the electronic structures of platinum(II) diimine complexes are strongly perturbed by solid-state effects, such as Pt...Pt and ligand...ligand intermolecular

interactions.^{8,9,13-15} While many examples of these materials have been prepared, the absence of structural information has, in most cases, limited interpretation of their spectroscopy. Indeed, until recently the red form of Pt(bpy)Cl₂ was the only structurally characterized example of a linear-chain platinum(II) diimine complex.¹⁰ However, because of several recent crystallographic studies¹⁵⁻²¹ there are now nine structurally characterized examples of neutral Pt(diimine)X₂ complexes with Pt...Pt separations ranging from 3.24 to 3.49 Å (see Chapter 3). This series of compounds affords the opportunity to correlate the spectroscopy of linear-chain platinum(II) diimine complexes with their crystalline structure. In this chapter, we demonstrate that the pronounced temperature dependence of the emission spectra of the red form of Pt(bpy)Cl₂ is attributable to a substantial contraction of the Pt chain at low temperature. Moreover, we find that the emission and absorption spectra of these linear-chain platinum(II) diimine compounds are consistent with an electronic structural model that considers the electronic properties of the ancillary ligands, as well as variations in the Pt...Pt separations.

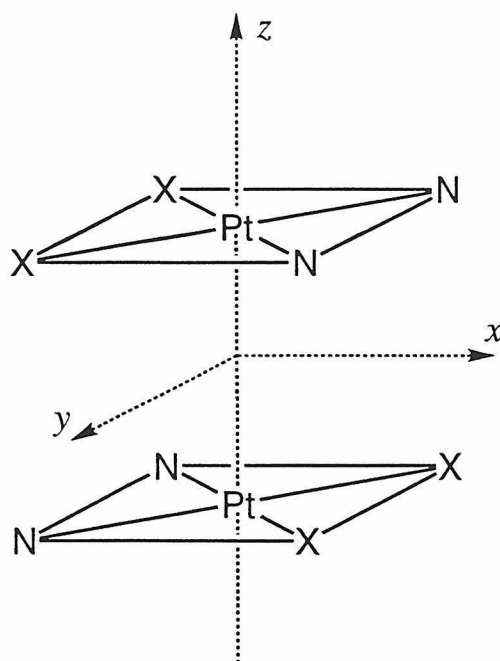
II. Experimental

The preparation of the linear-chain platinum(II) diimine complexes and the details of the X-ray crystallography are described in the experimental section of Chapter 3.

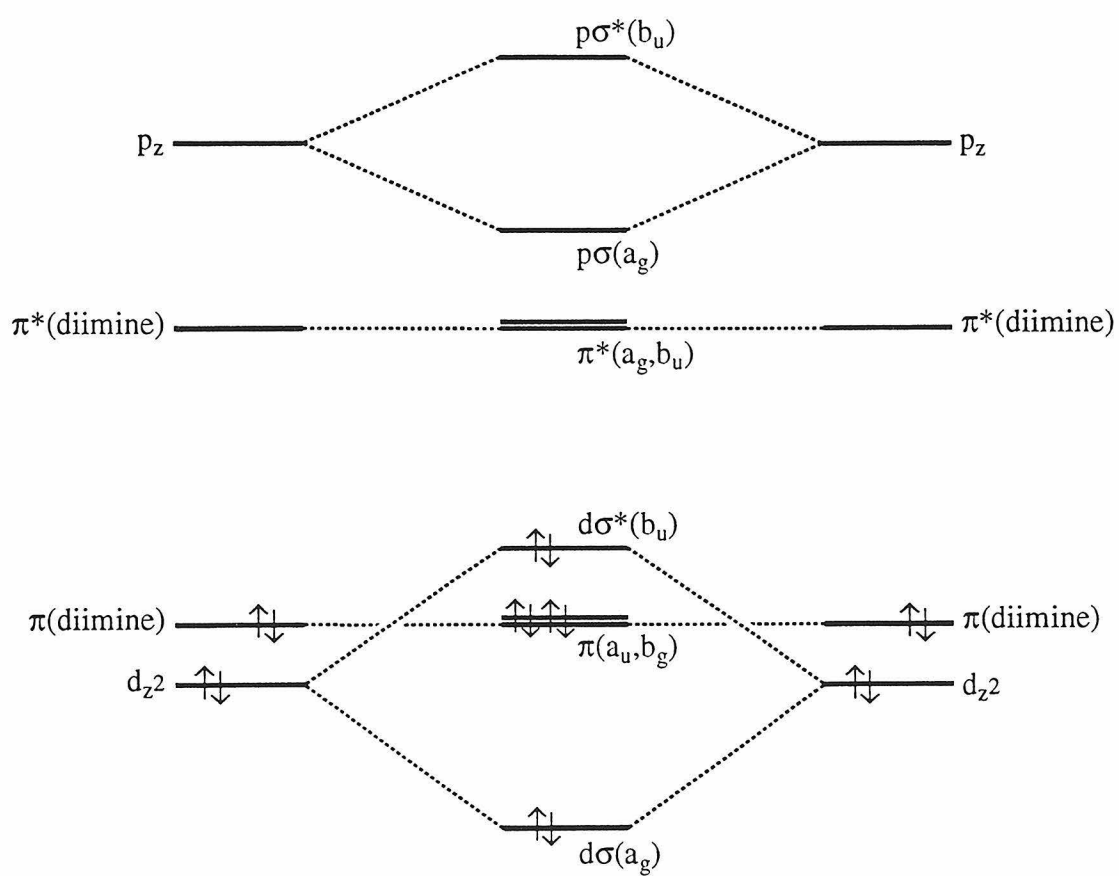
The instrumentation and techniques used for the spectroscopic and photophysical measurements are discussed in Chapter 2. We make several additional comments here. Suitable 77 K glassy solutions were obtained using a 10:10:1 ethanol:methanol:*N,N*-dimethylformamide (abbreviated as EMD) mixture as described by Bailey and co-workers.²² The sample was dissolved in *N,N*-dimethylformamide (dmf) and then diluted in the alcohol mixture. Rapid freezing of the sample in a quartz epr tube and the avoidance of mechanical stress or shocks resulted in crack-free glasses.

Figure 4.1 (a) Coordinate system used in the discussion of linear-chain platinum(II) diimine complexes. In this C_{2h} symmetry model, a single-repeat unit is composed of two stacked complexes mutually rotated by 180° about the chain axis. (b) Qualitative molecular orbital (MO) diagram for stacked platinum(II) diimine complexes. For simplicity, only the most relevant levels are depicted with their C_{2h} symmetry labels. The relative energies of the diimine $\pi^*(a_g, b_u)$ orbitals are not certain, though the a_g level may be somewhat stabilized by symmetry-allowed mixing with the $p\sigma(a_g)$ level. This MO scheme illustrates that with decreasing Pt...Pt distance, enhanced $5d_{z^2}\cdots 5d_{z^2}$ interaction will effectively raise the $d\sigma^*$ energy level, thereby reducing the $d\sigma^*-\pi^*$ energy gap.

(a)



(b)



Diffuse reflectance measurements were made on solid samples diluted in a MgSO_4 support; the samples were thoroughly ground before combining with MgSO_4 . The energies of the band maxima were found to be independent of concentration. For solid-state emission measurements of **1**, **7** and **9**, the samples were excited using the 457.9 nm line of a Spectra Physics 2020 5-W argon ion laser. In the case of $\text{Pt}(\text{bpy})(\text{NCO})_2$ (**9**), the 514.5 nm line was used for excitation and a GaAs photomultiplier tube was used for detection. The other instrumentation for this system is described in Chapter 2. Room-temperature solid-state emission spectra of **3**, **6** and **8**, as well as the 77 K glassy solution samples, were obtained using 313 or 366 nm excitation from a Hanovia 200 W Hg/Xe lamp and the corresponding detection apparatus described in Chapter 2.

III. Results and Discussion

A. Electronic Structure

The electronic structures of linear-chain platinum(II) diimine complexes, such as the red form of $\text{Pt}(\text{bpy})\text{Cl}_2$, are readily described using the molecular orbital (MO) model depicted in Figure 4.1. In this scheme, the orbitals of the platinum monomers are perturbed by interactions with adjacent platinum(II) complexes. The fully occupied $5d_{z^2}$ levels of adjacent metal centers split to give bonding ($d\sigma$) and antibonding ($d\sigma^*$) molecular orbitals. Similarly, the unoccupied $6p_z$ levels split to give $p\sigma$ and $p\sigma^*$ orbitals. For an extended chain, these discrete levels form bands whose width increases with the strength of the interaction between platinum centers. Because of the strong $\text{Pt}(d_{z^2})$ interaction, the HOMO is the predominantly metal-centered $d\sigma^*$ level. As shown later, the LUMO turns out to be the predominantly ligand-localized π^* orbital; we emphasize that this situation differs from that of the stacked $\text{Pt}(\text{CN})_4^{2-}$ complexes ($\text{Pt}\cdots\text{Pt}$ 3.1-3.7 Å) and binuclear d^8 complexes such as $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4+}$ ($\text{Pt}\cdots\text{Pt}$ 2.92 Å), where the LUMO is the predominantly metal-centered $p\sigma$ level. Thus, the colors of the platinum(II) diimine linear-chain complexes are due to an electronic transition to the

$^1\text{MLCT}[\text{d}\sigma^*(\text{Pt})\rightarrow\pi^*(\text{diimine})]$ state. It is apparent from this description that with decreasing Pt...Pt distance, enhanced $5\text{d}_{z^2}\cdots 5\text{d}_{z^2}$ interaction should stabilize the $^1\text{MLCT}[\text{d}\sigma^*\rightarrow\pi^*]$ state, thus the electronic transition to this state is predicted to shift to lower energy with decreasing Pt...Pt separation.

Single-crystal polarized absorption studies^{7,16,23,24} indicate that the electronic transition to the $^1\text{MLCT}[\text{d}\sigma^*\rightarrow\pi^*]$ state is strongly z -polarized - that is, polarized parallel to the chain axis ($\mathbf{E}\parallel\mathbf{c}$). The transition to the corresponding triplet state is x,y -polarized - that is, polarized perpendicular to the chain axis ($\mathbf{E}\perp\mathbf{c}$). The situation is quite similar to that of binuclear complexes such as $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ (Pt...Pt 2.92 Å), for which the transitions to the lowest $^1\text{A}_{2u}$ and $\text{E}_u(^3\text{A}_{2u})$ $\text{d}\sigma^*\rightarrow\text{p}\sigma$ states are z -polarized and x,y -polarized, respectively (double group D_{4h}).²⁵ We have derived selection rules by considering the symmetries of the orbitals that result from the interactions of two stacked platinum diimine complexes mutually rotated by 180° ; several of the compounds that we have studied (*e.g.*, $\text{Pt}(\text{bpy})\text{Cl}_2$) adopt this C_{2h} symmetric stacking arrangement (Figure 4.1; also see Chapter 3). The Pt levels (d_{z^2} and p_z) of the same symmetry combine as discussed above, and the HOMO is the $\text{d}\sigma^*(\text{b}_u)$. Similarly, symmetric and antisymmetric combinations of diimine π^* levels give rise to the two orbitals with a_g and b_u symmetry. Since the diimine orbitals of adjacent complexes have poor overlap, the relative energies of these levels is not obvious. In fact, the $\pi\rightarrow\pi^*$ transitions in these materials are essentially unperturbed from their monomer spectra.¹⁴ Notwithstanding, it seems likely that the $\pi^*(\text{a}_g)$ level is somewhat stabilized by symmetry-allowed mixing with the $\text{p}\sigma(\text{a}_g)$ level. The resulting spin-allowed electronic transition to the $^1\text{MLCT}[\text{d}\sigma^*(\text{b}_{1u})\rightarrow\pi^*(\text{a}_g)]$ state ($^1\text{B}_u$) is dipole-allowed with x and z polarization. (The transition involving the other π^* level, the b_u , is Laporte forbidden.) Electronic transitions to the spin-orbit components of the corresponding triplet states, $^3\text{B}_u$ (B_u , A_u , A_u) and $^3\text{A}_g$ (A_g , B_g , B_g in double group C_{2h}) are x,y,z -polarized and Laporte forbidden, respectively.

The predicted polarizations are consistent with the single-crystal spectroscopy; namely, the transition to the ${}^1\text{MLCT}[\text{d}\sigma^*(\text{b}_{1\text{u}})\rightarrow\pi^*(\text{a}_{\text{g}})]$ state is allowed with z -polarization and the corresponding spin-forbidden transition is allowed with x - and y -polarization. Unfortunately, because z and x share the same symmetry ($\text{b}_{1\text{u}}$) in the $\text{C}_{2\text{h}}$ point group, our model cannot distinguish between z - and x -polarizations - that is, any transition that is z -allowed, also is formally x -allowed. Descending to lower symmetry will not improve this situation. Gliemann and co-workers^{7,16,23,24} have skirted this problem by simply assigning the derived energy levels the $\text{C}_{2\text{v}}$ symmetry designations corresponding to a single complex. As a result, the x , y and z directions are distinct by symmetry. The transition to the ${}^1\text{B}_1$ $\text{d}\sigma^*\rightarrow\pi^*$ state is z -polarized and the transitions to the A_1 , A_2 and B_2 (${}^3\text{B}_1$) triplet $\text{d}\sigma^*\rightarrow\pi^*$ states are x -polarized, forbidden and y -polarized, respectively. A similar result is obtained if $\text{D}_{2\text{h}}$ symmetry is assumed with a lowest a_{g} π^* level; then electronic transitions to the ${}^1\text{B}_{1\text{u}}$ $\text{d}\sigma^*\rightarrow\pi^*$ state are z -polarized and those to the corresponding $\text{B}_{3\text{u}}$, $\text{A}_{1\text{u}}$ and $\text{B}_{2\text{u}}$ (${}^3\text{B}_{1\text{u}}$) triplets are x -polarized, forbidden and y -polarized, respectively. However, because both of these approaches ignore the true symmetry of the stacks, the models are not rigorous.

Therefore, in contrast to cases of stacked $\text{Pt}(\text{CN})_4^{2-}$ complexes and binuclear d^8 complexes, we conclude that a strict group theoretical analysis does not predict that the transition to the ${}^1\text{MLCT}[\text{d}\sigma^*\rightarrow\pi^*]$ state is *uniquely* z -polarized since the molecular z -polarization can in principle mix with y -polarization. The fact that this transition is experimentally observed to be strongly z -polarized indicates that the corresponding transition dipole is parallel or nearly parallel to the chain axis; thus, there is a close analogy between the lowest excited states of the diimine linear chains and other stacked d^8 systems. We also emphasize that in each case we have considered, mixing of the diimine π^* level with the $\text{p}\sigma$ level is symmetry allowed and expected to enhance the oscillator strength of the $\text{d}\sigma^*\rightarrow\pi^*$ transitions; π^* - p_z mixing is well-established in platinum(II) polypyridyl complexes.²⁶

In actual fact, a better description of weakly interacting d^8 systems is given by a valence bond (VB) model.²⁷ Both the MO and VB models account for excited states strongly stabilized with respect to those of the monomeric analogs. However, the VB model also describes observed states which are only weakly perturbed from those of the monomer, and predicts half of the excited states to be energetic ionic states arising from metal-to-metal charge transfers. There are no corresponding states in the MO model. Nevertheless, in the case of d^8 dimers the MO model gives a reasonable description of the lowest $d\sigma^* \rightarrow p\sigma$ excited states. For example, the large excited-state distortions along the metal-metal axis in d^8 dimers is consistent with increased metal-metal bonding in the $d\sigma^* \rightarrow p\sigma$ excited states.^{27,28} In addition, the VB treatment does not seriously alter the MO explanation of the spectroscopy of these systems or our understanding of their thermal chemistry and photochemistry. Thus, for simplicity the MO description is adopted here.

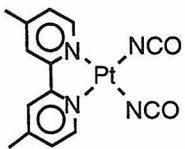
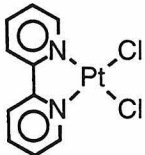
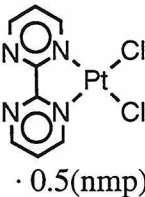
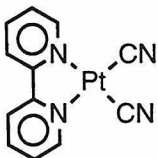
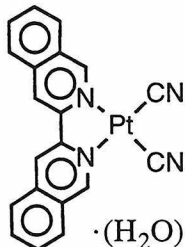
B. Spectroscopy

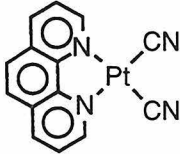
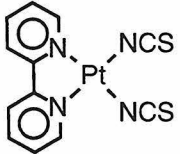
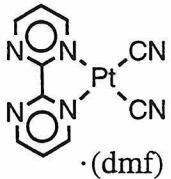
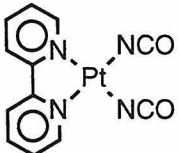
The spectroscopic properties of nine structurally characterized platinum(II) diimine complexes (**1-9**) are summarized in Table 4.1. Though we have not examined $\text{Pt}(i\text{-biq})(\text{CN})_2 \cdot \text{H}_2\text{O}$ (**5**) ($i\text{-biq}$ =3,3'-biisoquinoline) in our laboratory, the structure and spectroscopy²⁰ of **5** are similar to those of the other compounds in Table 4.1.²⁹

1. Absorption

Each of these materials is intensely colored in the solid state because of an electronic transition to the $^1\text{MLCT}[d\sigma^*(\text{Pt}) \rightarrow \pi^*(\text{diimine})]$ state.^{8,9,13,14} With decreasing $\text{Pt} \cdots \text{Pt}$ distance, enhanced $5d_{z^2} \cdots 5d_{z^2}$ interaction causes a red-shift in this transition, and the color changes from orange to blue (Figure 4.1). Diffuse reflectance spectra of these compounds provide a measure of this wide variation in color (Figure 4.2a). The maximum of the $^1d\sigma^* \rightarrow \pi^*$ band in blue $\text{Pt}(\text{bpy})(\text{NCO})_2$ (**9**) ($\text{Pt} \cdots \text{Pt}$ 3.24 Å) is shifted to lower energy by nearly 5000 cm^{-1} from that of orange $\text{Pt}(\text{dmbpy})(\text{NCO})_2$ (**1**) ($\text{Pt} \cdots \text{Pt}$ 3.49

Table 4.1. Photophysical properties^a of linear-chain platinum(II) diimine complexes.

	Compound (color)	Reflectance Maximum (nm)	Emission Maximum (nm)	Emission fwhm (cm ⁻¹)	Emission Lifetime (ns)
	[Average Pt...Pt, Å]				
1	 Pt(dmbpy)(NCO) ₂ (orange) [3.49] ^{18,19}	480(sh)	602 (604, 10 K)	3150 (2940, 10 K)	110 (280)
2	 Pt(bpy)Cl ₂ (red) [3.45] ^{10,30}	516	613 (651, 10 K)	2000 (1050, 10K)	155 ^b
3	 Pt(bpm)Cl ₂ ·0.5(nmp) (red) [3.39]	531	684	2450	—
4	 Pt(bpy)(CN) ₂ (red) [3.35] ^{15,31}	481	600 (655, 30 K)	1500 (1020, 30 K)	160 ^b
5	 Pt(<i>i</i> -biq)(CN) ₂ (orange-red) [3.34] ²⁰	—	627 ^c	—	—

6		Pt(phen)(CN) ₂ (violet) [3.34]	506	715 (775, 30 K)	2300 (960, 30 K)	130 ^b
7		Pt(bpy)(NCS) ₂ (red) [3.30]	525	664 (690, 10 K)	2070 (1860, 10 K)	80 (225)
8		Pt(bpm)(CN)·(dmf) (red) [3.28] ¹⁶	536	641	2200	~100 ^d
9		Pt(bpy)(NCO) ₂ (blue) [3.24] ¹⁷	604	780 (823, 10 K)	1500 (1400, 10 K)	—

^a Data recorded at room temperature unless otherwise noted (values in parentheses).

^b Emission and lifetime data from references 14 and 8.³²

^c Data from reference 20.

^d Emission lifetime from reference 16.

Figure 4.2 Diffuse reflectance data displayed as absorption spectra for compounds **1-9**.³³ The spectra are stacked in order of Pt···Pt separation for purposes of comparison. Spectra for the yellow forms of Pt(dmbpy)(NCO)₂ and Pt(bpy)Cl₂ are outlined in dots. Data for **5** are not shown.²⁹

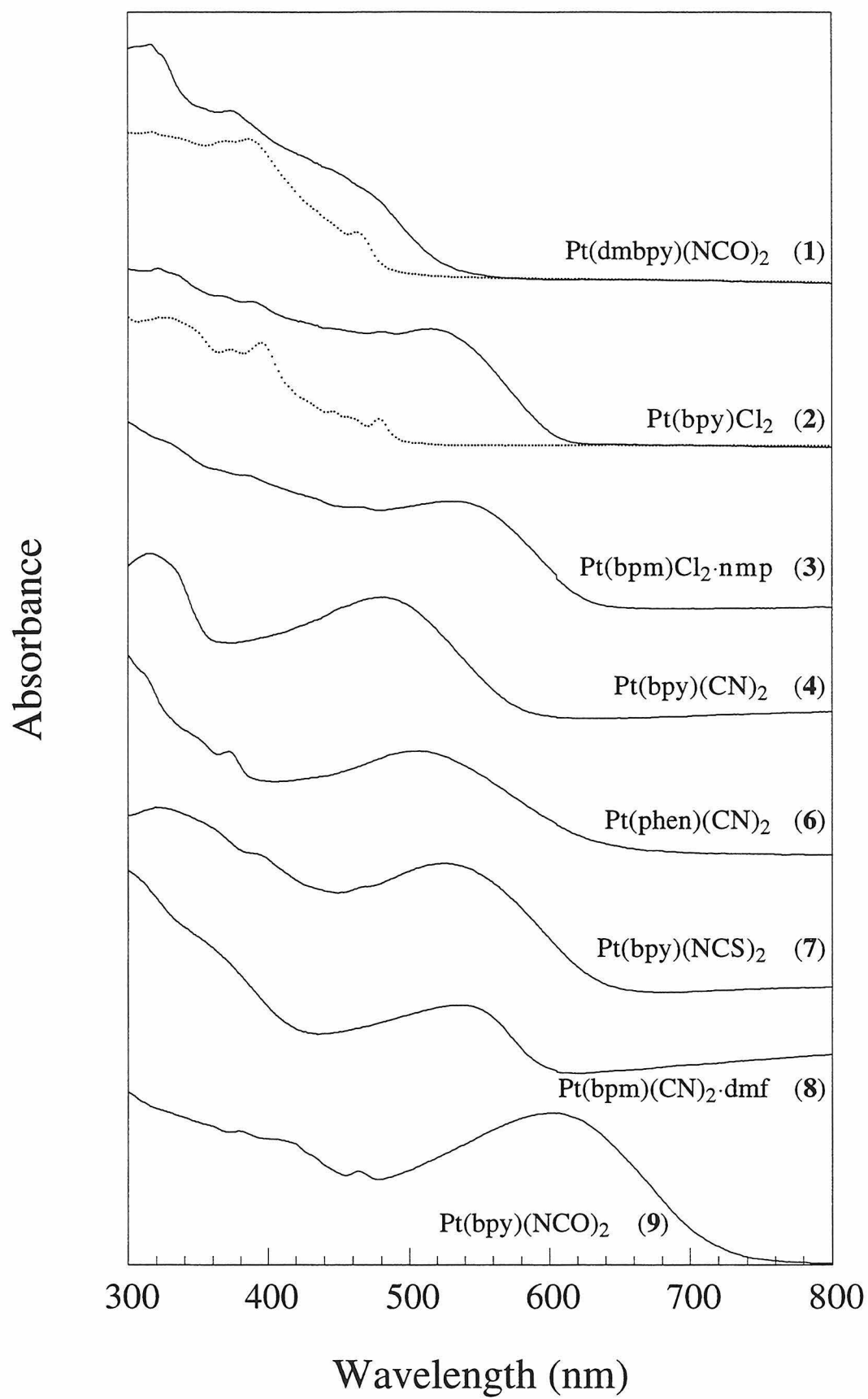
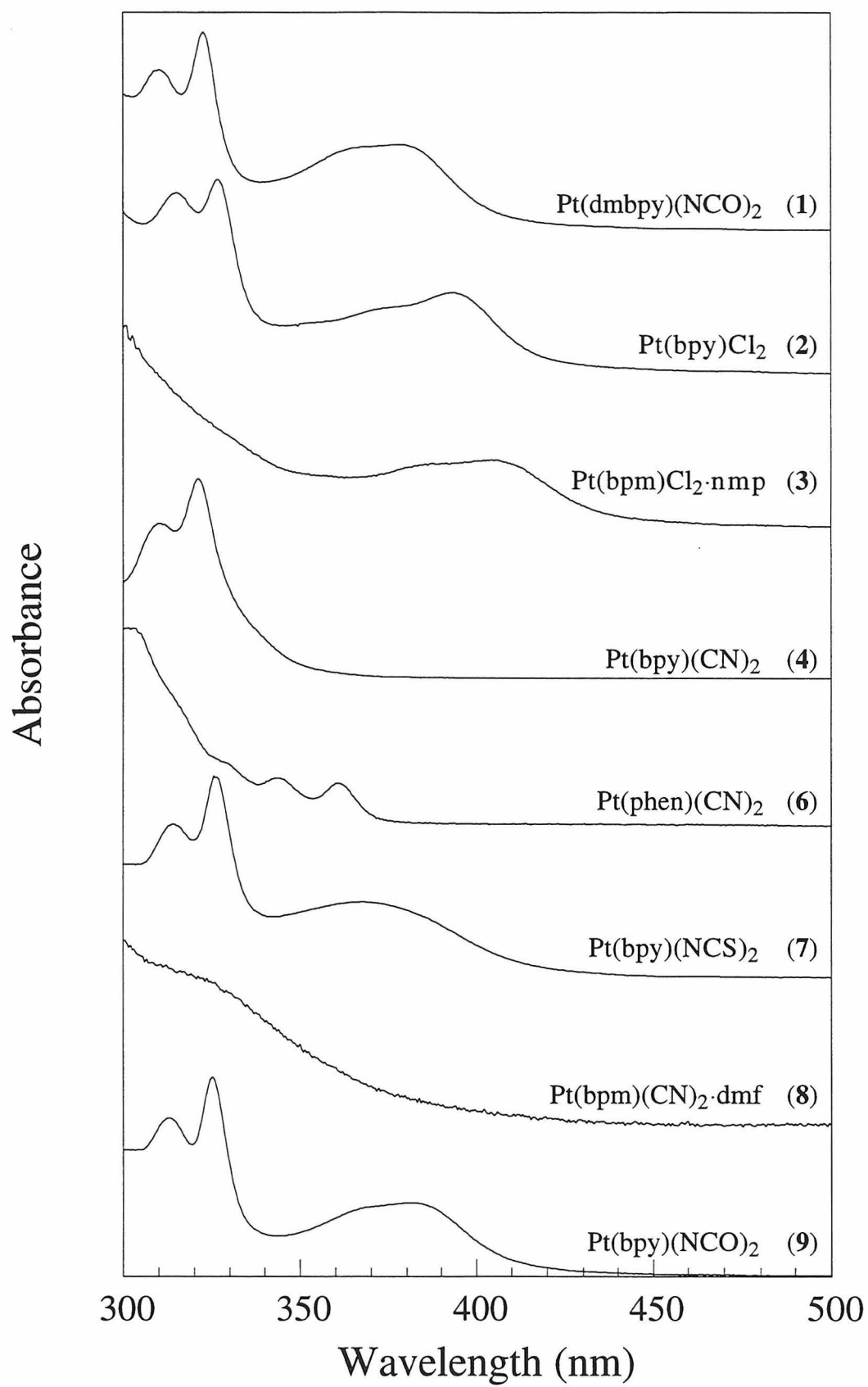


Figure 4.3 Absorption spectra for compounds **1-9** in *N*-methyl-pyrrolidinone (nmp) solution. The spectra are stacked for purposes of comparison. Data for **5** are not shown.²⁹



Å). The transition to the corresponding triplet is presumably buried in the low-energy flank of this band and has been resolved in emission excitation spectra of **4** and **6**, shifted $\sim 2500\text{ cm}^{-1}$ to lower energy of the reflectance maximum.¹⁴ Our electronic structural model also is qualitatively consistent with the yellow colors of the polymorphs of Pt(bpy)Cl₂ and Pt(dmbpy)(NCO)₂, because their shortest Pt···Pt contacts are greater than 4.4 Å. At shorter wavelengths (300-400 nm), intraligand and MLCT features are observed; these can be assigned based on comparison with solution absorption data (*vide infra*). For **2-4, 7**, and **9**, a spin-forbidden $\pi \rightarrow \pi^*$ transition is resolved near 460 nm; the position of this band is unperturbed from that observed in solution spectra, as well as reflectance spectra of related complexes with no short Pt···Pt contacts. (In the spectrum of **9**, the poorly resolved structure near 430 nm is tentatively assigned to a unimolecular spin-forbidden MLCT transition.)

We have observed that crystals of **1-4** and **6-8** are strongly dichroic;^{29,34} light polarized parallel to the Pt chains (**E**||**c**) is more intensely absorbed than light polarized perpendicular to the Pt chains (**E**⊥**c**). For example, when viewed under a microscope using transmitted light, needles of Pt(bpy)(NCS)₂ (**7**) appear very dark red with **E**||**c** and pale red with **E**⊥**c**. For compounds **2**, **4**, **6**, and **8**, Gliemann and co-workers^{7,16,23,24} have reported single-crystal polarized absorption spectra. A temperature-sensitive, low-energy $d\sigma^* \rightarrow \pi^*$ band is observed in the **E**⊥**c** spectrum ($\epsilon \sim 100\text{-}250\text{ M}^{-1}\text{ cm}^{-1}$).³⁵ This feature has been attributed to a spin-forbidden transition. However, the maximum of this band usually occurs shifted, only slightly, to lower energy of our diffuse reflectance maxima, which correspond to the spin-allowed transition. For example, the band maximum in the room-temperature **E**⊥**c** spectra of Pt(bpy)Cl₂ (**2**) and Pt(bpy)(CN)₂ (**4**) is shifted to lower energy by only $\sim 200\text{ cm}^{-1}$ and $\sim 800\text{ cm}^{-1}$, respectively, from the corresponding reflectance maxima. However, emission excitation spectra of **4** and **6** suggest that the spin-forbidden $d\sigma^* \rightarrow \pi^*$ transition is shifted $\sim 2500\text{ cm}^{-1}$ to lower energy of the corresponding singlet; indeed, this shift is more typical of singlet-triplet splittings

for stacked d^8 systems.^{2,27,28} It is possible that the $E_{\perp c}$ spectra are contaminated with the spin-allowed $d\sigma^* \rightarrow \pi^*$ transition, and consequently, the band maxima may be poor indicators of the energy of the triplet absorptions (at least at room-temperature). With decreasing temperature, lattice contraction causes the band to shift to lower energy; typically, the band shifts 1000 cm^{-1} from 295 to 10 K - as observed in the unpolarized emission spectra (*vide infra*). Interestingly, in the $E_{\perp c}$ spectrum of $\text{Pt}(\text{bpm})(\text{CN})_2 \cdot \text{dmf}$ (**8**) at 10 K, a shoulder is clearly visible, shifted by $\sim 1400\text{ cm}^{-1}$ to higher energy of the parent peak; this vibronic structure is diagnostic of involvement of the bpm ligand in the electronic transition. The peak energy of the low energy band in the $E_{\parallel c}$ spectrum has never been determined because the crystals are too strongly absorbing.^{7,16,23,24} The strong $E_{\parallel c}$ polarization of the $^1d\sigma^* \rightarrow \pi^*$ transitions is consistent with our group theoretical considerations.

Each of the solids in Table 4.1 dissolves to give yellow or colorless solutions confirming that the intense colors of these materials are attributable to intermolecular interactions (Figure 4.3ab). The solution absorption spectra are characteristic of square planar platinum(II) diimine complexes as described in Chapter 2. Solvent insensitive $\pi \rightarrow \pi^*$ vibronic structure near 320 nm is evident in the spectra of the bipyridyl complexes. In the case of $\text{Pt}(\text{phen})(\text{CN})_2$, the lowest spin-allowed intraligand transitions originate near 360 nm; the spectrum in the 300-500 nm region is almost identical with those of $\text{Pt}(\text{phen})_2^{2+}$ and $\text{Rh}(\text{phen})_3^{2+}$.^{13,36} The lowest $^1\text{MLCT}[d\pi \rightarrow \pi^*]$ absorption band occurs between 330 and 405 nm (range $\sim 5500\text{ cm}^{-1}$), shifting to lower energy with decreasing solvent polarity. The maximum of this band for $\text{Pt}(\text{bpy})\text{Cl}_2$ (**2**) occurs at 392 nm in nmp solution; for the remaining compounds, the maximum varies over the 330-405 nm range depending the pseudohalide and diimine ligands. The origin of the variations are, at least qualitatively, understandable. The different diimine ligands effectively tune the energy of the MLCT states by shifting the energy of the ligand π^* level, and, to a lesser extent, perturbing the platinum d levels. The ancillary ligands exert

their influence by perturbing the metal d levels. As expected, the band is shifted to lower energy with stronger π -acceptor ligands (*e.g.*, bpm vs bpy). Similarly, the complexes with the strongest electron donating ancillary ligands (*e.g.*, Cl^-) have lower energy MLCT transitions. In the case of the dicyano complexes, the lowest monomer MLCT band is shifted 4-5000 cm^{-1} to higher energy of the corresponding dichloro complex; this band is not well-resolved. For comparison, the maximum of the MLCT band for $\text{Ru}(\text{bpy})_2(\text{CN})_2$ (460 nm, CH_3OH) is shifted 3500 cm^{-1} to higher energy of the corresponding band for $\text{Ru}(\text{bpy})_2\text{Cl}_2$ (555 nm, CH_2Cl_2).³⁷

2. Emission

At room temperature, each of the materials listed in Table 4.1 (**1-9**) exhibits characteristically intense emission that originates from a lowest $^3\text{MLCT}[\text{d}\sigma^*(\text{Pt}) \rightarrow \pi^*(\text{diimine})]$ state (Figure 4.4). In accord with the triplet assignment, the room-temperature excited-state lifetimes are 100-300 ns;³⁸ the radiative rate constants (k_r) are on the order of 10^5 s^{-1} (*e.g.*, $\text{Pt}(\text{bpy})(\text{CN})_2$, 2.6×10^5 ; $\text{Pt}(\text{phen})(\text{CN})_2$, $1.8 \times 10^5 \text{ s}^{-1}$).^{8,14} As expected, the emission band shifts to lower energy with decreasing Pt...Pt distance, because enhanced $5\text{d}_{z^2} \cdots 5\text{d}_{z^2}$ interaction decreases the $\text{d}\sigma^*-\pi^*$ gap. For example, the band maximum for **9** (Pt...Pt 3.24 Å) is nearly 3800 cm^{-1} lower in energy than that of **1** (Pt...Pt 3.49 Å); in fact, the emission from **9** is the lowest-energy emission that we have observed for platinum(II) diimine chains. The band profiles are characteristically narrow (fwhm $\sim 2000 \text{ cm}^{-1}$ at 300 K) and asymmetric; the Stokes shift between the diffuse reflectance and emission maxima is 4000-5000 cm^{-1} (average, $4.0(9) \times 10^3 \text{ cm}^{-1}$).³² With decreasing temperature, the band further narrows and shifts sharply to lower energy. As shown in Figure 4.5, the emission maximum of $\text{Pt}(\text{bpy})(\text{NCO})_2$ (**9**) red shifts by 750 cm^{-1} when a crystalline sample is cooled from room temperature to 10 K. This thermochromism is attributable to a substantial contraction of the Pt chain at low temperature, as discussed in the next section.

Figure 4.4 Room-temperature solid-state emission spectra for compounds **1-9**. The spectra are stacked in order of Pt...Pt separation for purposes of comparison. (Data for **5** are not shown.²⁹ The structure in the spectra of **3**, **6**, and **8** are due to a diffraction grating anomaly.)

Emission Intensity

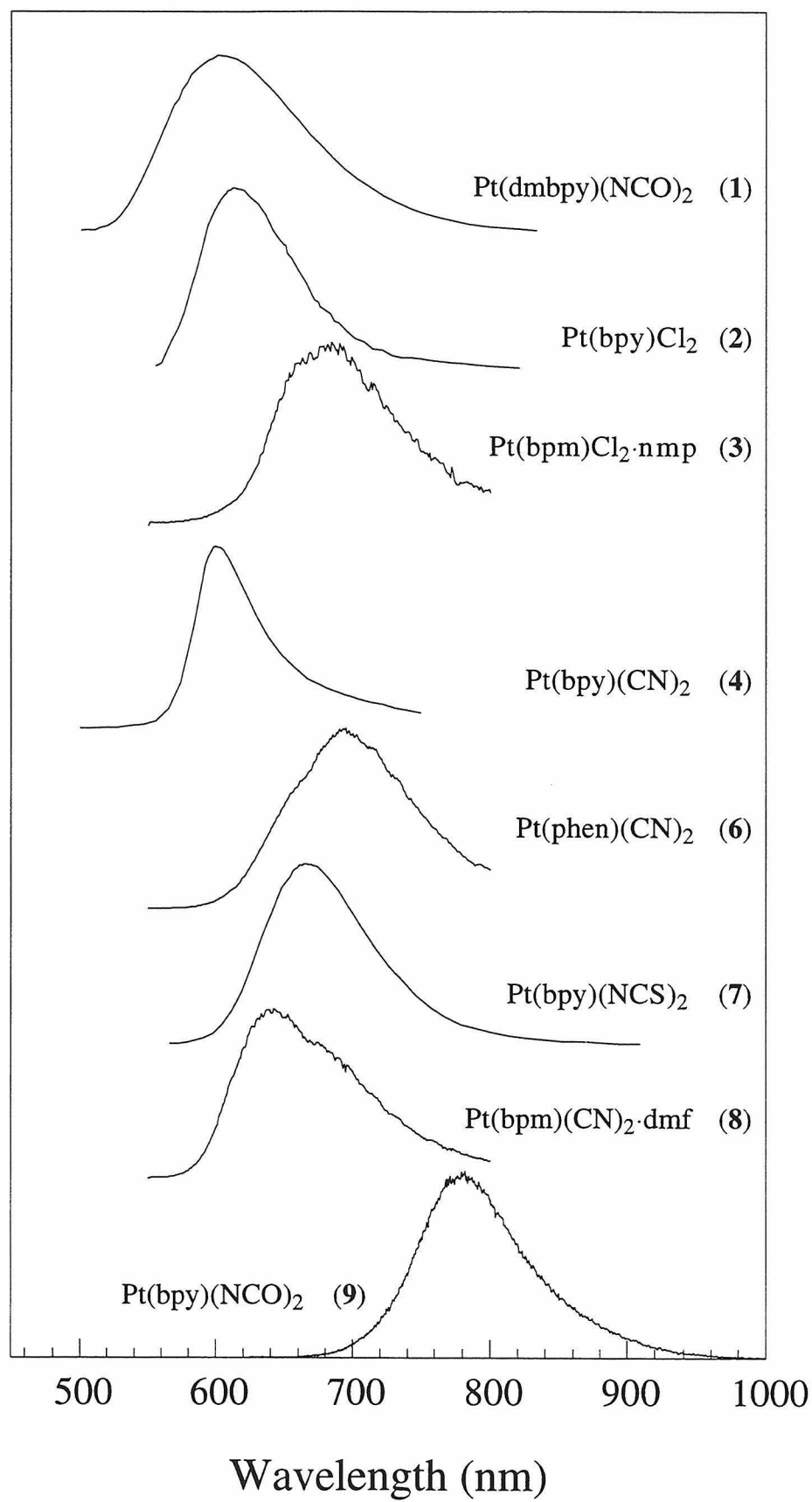
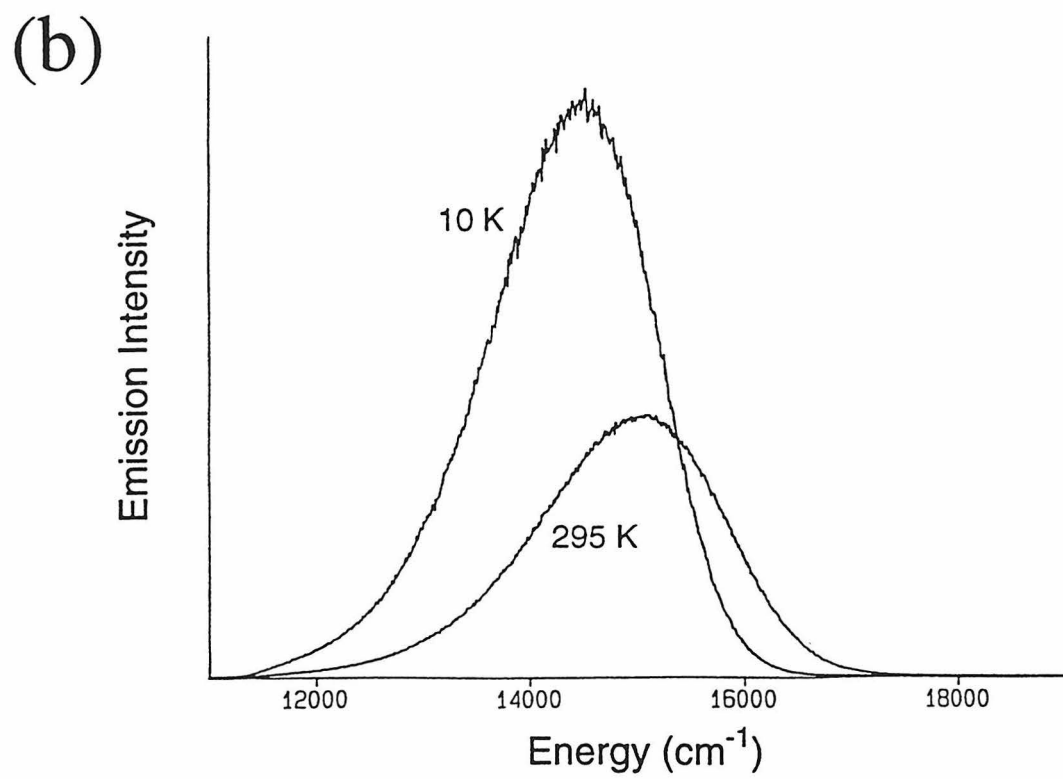
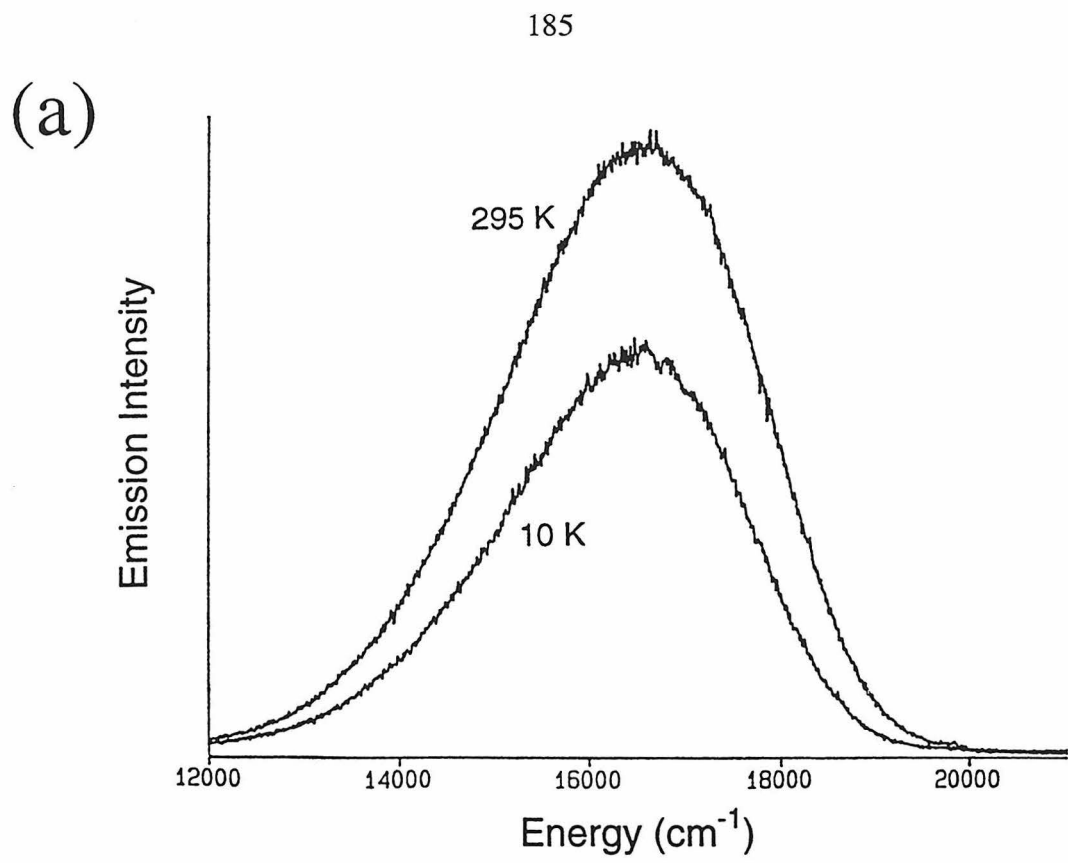


Figure 4.5 Room-temperature and 10 K emission spectra for microcrystalline samples of (a) Pt(dmbpy)(NCO)₂ (**1**), (b) Pt(bpy)(NCS)₂ (**7**), and (c) Pt(bpy)(NCO)₂ (**9**) (λ_{ex} =457.9 nm). In the cases of **1** and **9**, the relative intensities of the spectra at different temperatures are not meaningful.



(c)

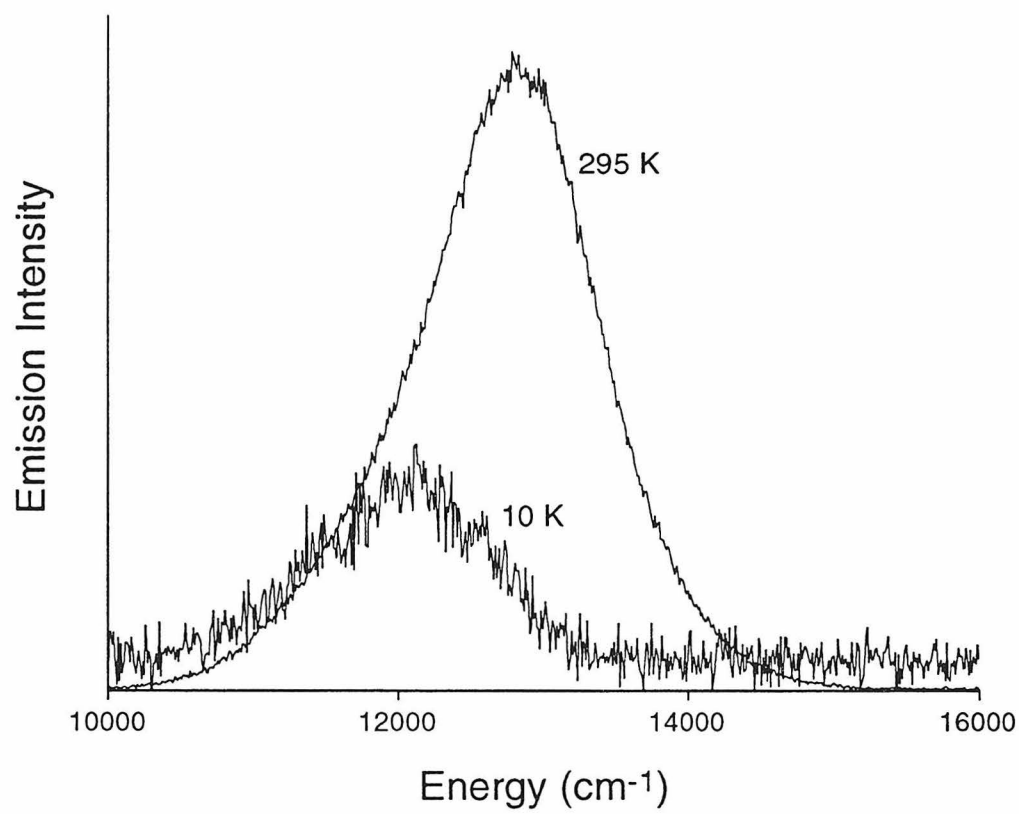


Figure 4.6 Emission spectra for compounds **1-9** in glassy EMD solution at 77 K ($\lambda_{\text{ex}}=313$ nm). The spectra are stacked for purposes of comparison. Spectra for **1** in acetone-toluene (1:1) (acet-tol) and 2-methyl-tetrahydrofuran (2-Me-thf) glassy solutions at 77 K also are shown. (Data for **5**²⁹ and **6** are not shown.)

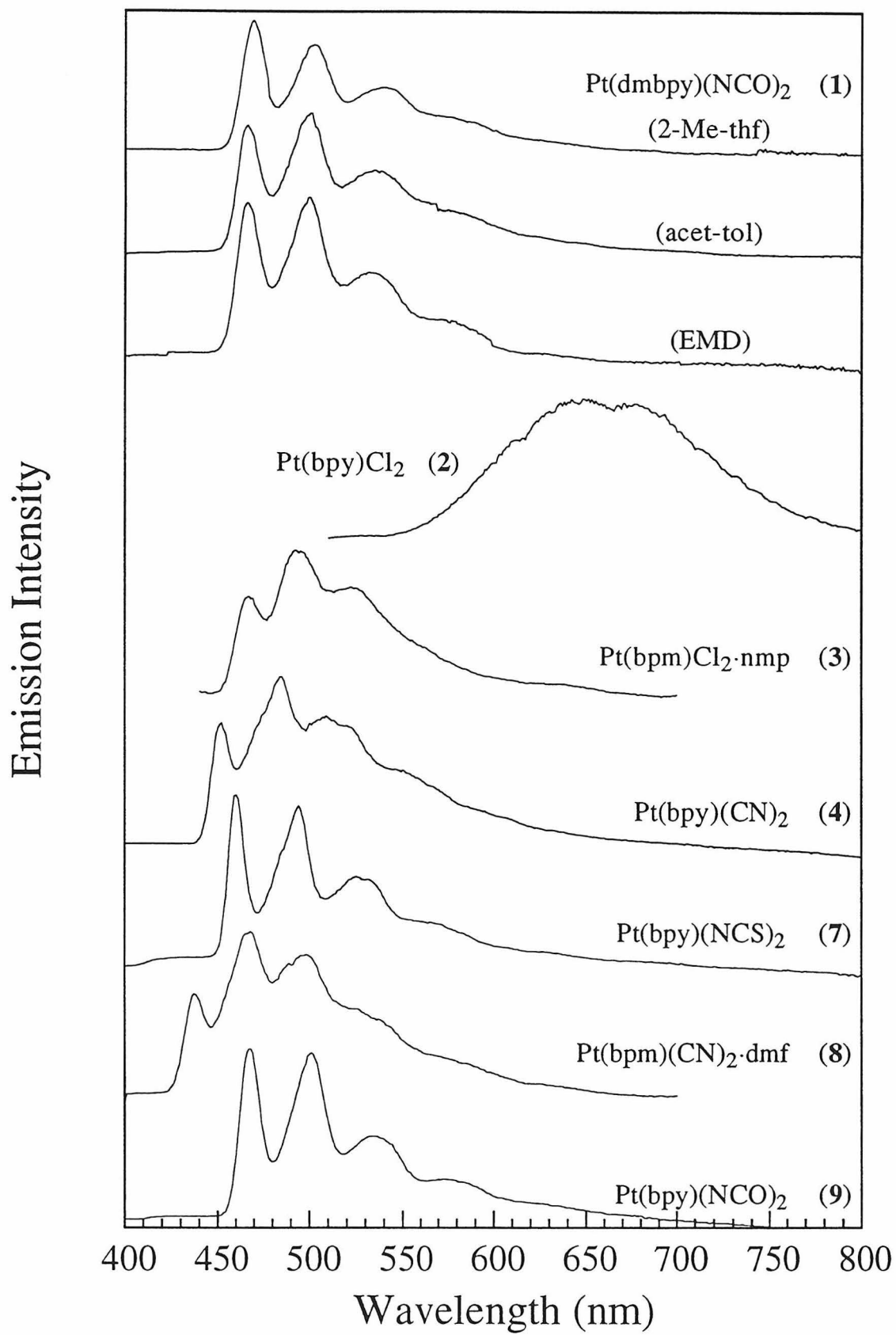
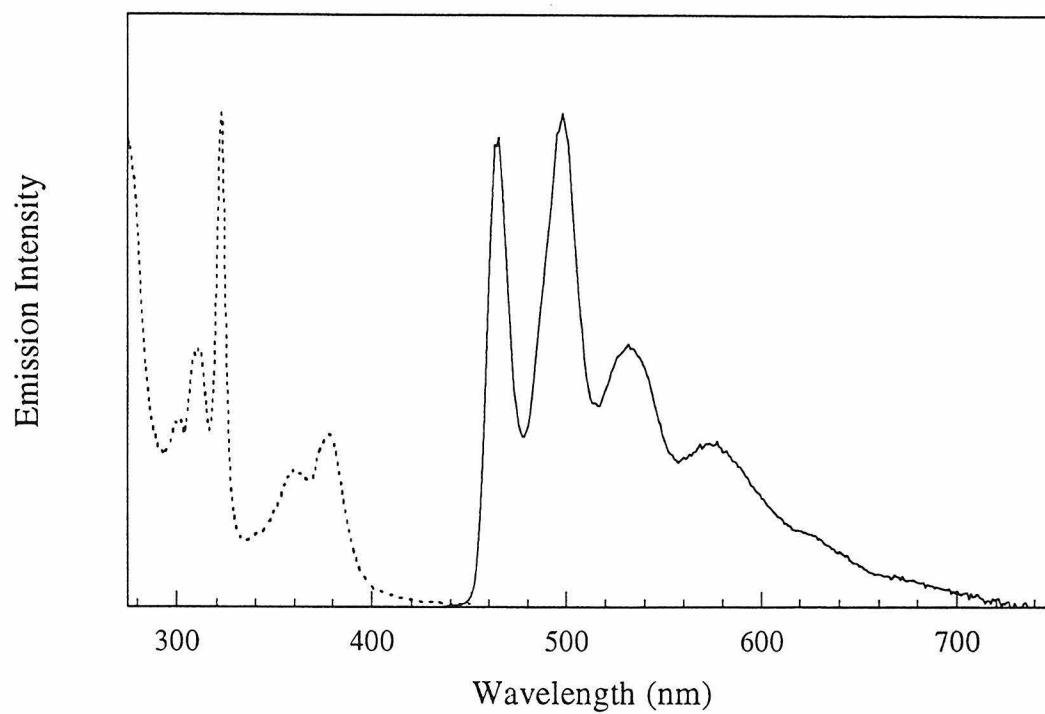
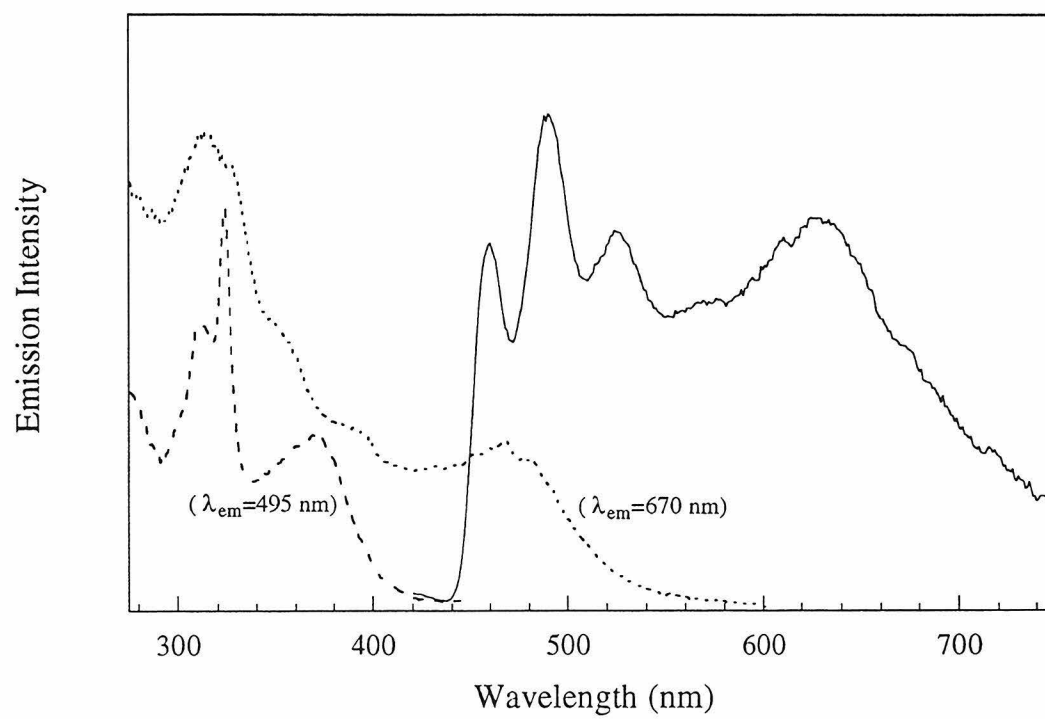


Figure 4.7 (a) Emission and excitation spectra for $\text{Pt}(\text{bpy})(\text{NCO})_2$ (**9**) in dilute glassy EMD solution at 77 K (λ_{ex} =313; λ_{em} =498 nm). (b) Emission and excitation spectra for $\text{Pt}(\text{bpy})(\text{NCS})_2$ (**7**) in a concentrated glassy EMD solution at 77 K (λ_{ex} = 313; λ_{em} =495 and 670 nm).

(a)



(b)



For compounds **2**, **4**, **6**, and **8**, Gliemann and co-workers^{7,16,23,24} have reported single-crystal polarized emission spectra. The maximum of the **E_{llc}** emission band is $\sim 1000\text{ cm}^{-1}$ higher in energy than the maximum of the **E_{lc}** band. Even at low temperature, the **E_{llc}** luminescence spectrum decays in $< 3\text{ ns}$ as expected for a spin-allowed process involving the $^1\text{MLCT}[\text{d}\sigma^* \rightarrow \pi^*]$ state. The lifetime of the **E_{lc}** emission is on the order of 100 ns at room temperature and 2 ms at 2 K ,³⁸ as expected for emission from the $^3\text{MLCT}[\text{d}\sigma^* \rightarrow \pi^*]$ state. In fact, the maxima of the room temperature **E_{lc}** emission bands roughly agree with those of our unpolarized emission data.^{32,39} These polarizations also are consistent with group theoretical considerations. Interestingly, while compounds **2**, **4** and **8** adopt the C_{2h} symmetry stacking arrangement shown in Figure 4.1, the chains in $\text{Pt}(\text{phen})(\text{CN})_2$ (**6**) have lower symmetry. Adjacent $\text{Pt}(\text{phen})(\text{CN})_2$ units are mutually rotated by 137° and are tilted by 84° with respect to the chain axis (see Chapter 3). Thus, the increased depolarization observed in the emission spectra of **6**²⁴ is attributable, at least in part, to an increased perpendicular component of the transition dipole caused by the tilting of the planar complexes from a 90° orientation with respect to the chain axis.

In 77 K frozen solution, compounds **1-9** give rise to emission spectra (Figures 4.6-4.7) characteristic of monomeric platinum(II) diimine complexes as discussed in Chapter 2. Thus, the emission originates at higher energy than in the spectra of the linear-chain forms. The excitation spectra for dilute frozen solutions agree with the solution absorption spectra (Figure 4.7). In the case of relatively strong-field ancillary ligands (CN^- , NCS^- , NCO^-), the emission profile is highly structured and the lowest excited state clearly is a ligand-localized $^3\pi \rightarrow \pi^*$ state.²⁹ In the case of $\text{Pt}(\text{dmbpy})(\text{NCO})_2$ (**1**), the Franck-Condon factors are somewhat solvent sensitive, but the emission energy is solvent insensitive, as expected. The broad red emission in the spectrum of $\text{Pt}(\text{bpy})\text{Cl}_2$ (**2**) originates from a lowest spin-forbidden ligand field state.⁴⁰ Not surprisingly, the yellow polymorphs of $\text{Pt}(\text{bpy})\text{Cl}_2$ ¹³ and $\text{Pt}(\text{bpy})(\text{NCO})_2$ – with

shortest Pt...Pt contacts longer than 4.4 Å – exhibit emission spectra similar to those obtained from frozen solution. For several of these compounds (**1**, **7** and **9**), the frozen solution emission profile changes dramatically with increasing concentration, and a new emission feature is resolved near 600-700 nm. The corresponding excitation spectra show an additional low-energy band maximizing at wavelengths *longer* than the 450 nm origin of the monomer $^3\pi\rightarrow\pi^*$ emission (Figure 4.7). Since the new excitation and emission maxima do not exactly match the solid-state spectra, these results cannot be entirely explained by precipitation. Bailey and co-workers²² have studied similar concentration effects on the frozen solution emission spectra of chloro(terpyridine)platinum(II). In analogy to their work, we attribute the new emission and absorption features to the formation of dimers and oligomers.

C. Temperature Dependence of the Emission Spectrum of $Pt(bpy)Cl_2$

The temperature dependence of the emission spectrum of the red form of crystalline $Pt(bpy)Cl_2$ is striking (Figure 4.8a).^{7-9,13} At room temperature, there is a relatively narrow (2000 cm^{-1} fwhm) and asymmetric band with a maximum at 613 nm (16300 cm^{-1}). With decreasing temperature, this band sharply narrows and red-shifts, and, at 10 K, the peak is at 651 nm (15350 cm^{-1} ; 1050 cm^{-1} fwhm). In addition, a distinctive shoulder is resolved approximately 1500 cm^{-1} further to the red of the 15350 cm^{-1} peak at 10 K. Vibronic structure with this spacing is diagnostic of involvement of the bipyridyl ligand in the electronic transition.⁹ Interestingly, in the single-crystal polarized absorption spectrum, the lowest-energy feature also shows a marked temperature dependence, strongly red-shifting ($\sim 1100\text{ }cm^{-1}$) as the temperature is lowered from 298 to 10 K; a vibronic feature approximately 1500 cm^{-1} to higher energy exhibits similar behavior.⁷ These observations are consistent with a $^3MLCT[d\sigma^*\rightarrow\pi^*(bpy)]$ emissive state.

The thermochromic properties are related to the temperature dependence of the structure of Pt(bpy)Cl₂ discussed in detail in Chapter 3. In these crystals, the square planar molecules stack along the *c* axis. Successive complexes are rotated by 180° so that eclipsing of the ligands is avoided and the Pt···Pt···Pt chain is slightly zigzag. The most important change in the crystal structure with decreasing temperature is a substantial anisotropic contraction of the unit cell. Upon cooling from room temperature to 20 K, the lengths of all three unit-cell edges decrease; the length of the *c* axis exhibits the greatest thermal sensitivity, decreasing to 97.6% of the room-temperature value at 20 K; the corresponding unit-cell volume is 97.0% of the room-temperature volume. The cooling-induced contraction of the *c* axis is accompanied by a shortening of the intermolecular contacts between stacked complexes. Thus, at 20 K, the intermolecular spacing of 3.322(2) Å (= *c*/2) and the Pt···Pt distance of 3.370(2) Å are significantly shorter than the room-temperature values of 3.402(1) and 3.449(1) Å. The temperature (*T*) dependence of the Pt···Pt separation (*R*) between 20 and 294 K is given by:

$$R_{\text{Pt-Pt}} = 3.3657 + 0.000170(T) + 3.72 \times 10^{-7}(T)^2 \quad (4.1)$$

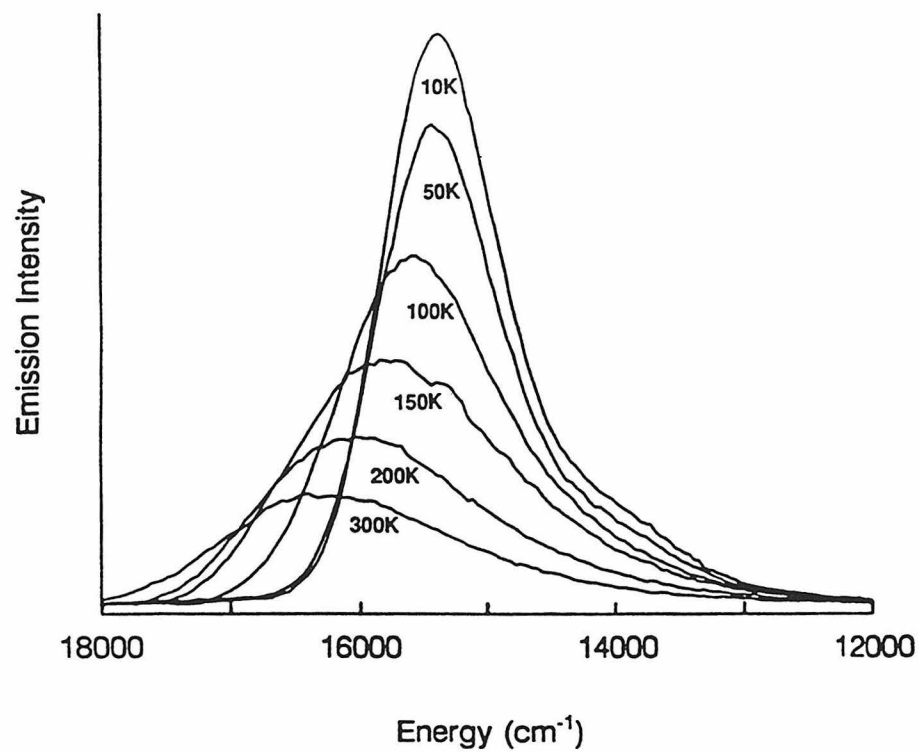
where *R* and *T* are in units of Å and K, respectively.

This lattice contraction enhances the electronic coupling between stacked Pt(bpy)Cl₂ units; as the temperature is lowered from 294 to 20 K, there is a 0.08 Å shrinkage of the Pt···Pt distance, resulting in a smaller dσ*(Pt)–π*(bpy) energy gap. In Figure 4.8b, the emission peak energies^{8,9} at temperatures from 300 to 10 K are plotted as a function of *R*⁻³, where *R* has been estimated using equation (4.1).⁴¹ The emission maximum (*v*_{max}) exhibits an approximately linear dependence on *R*⁻³; given by equation (2),

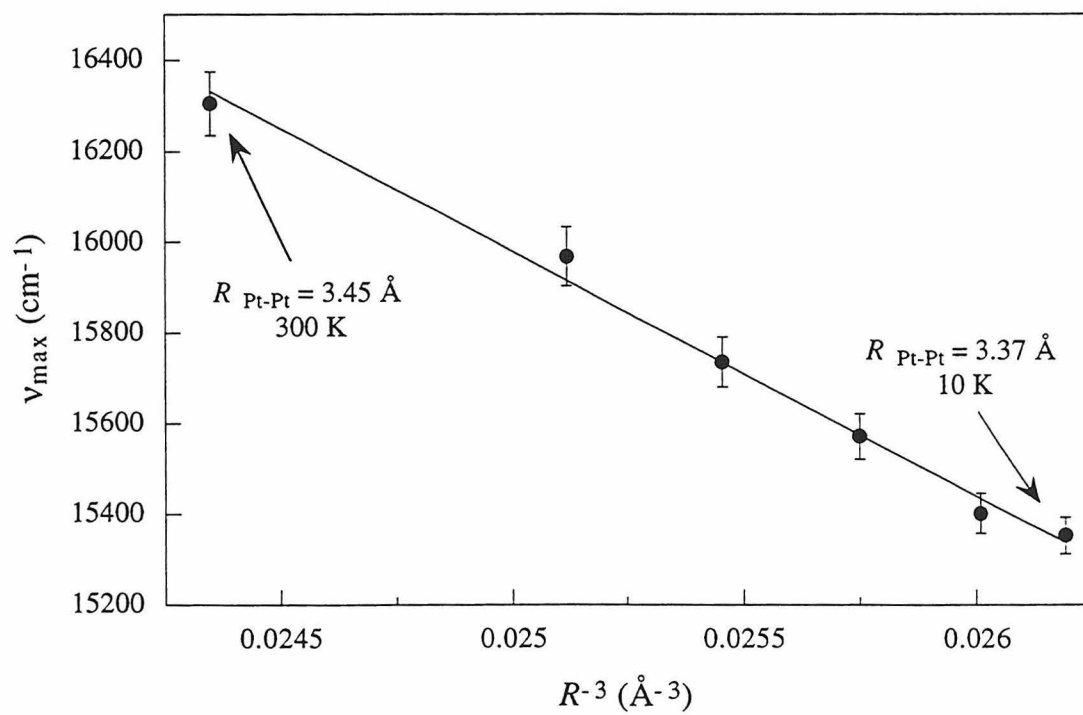
$$v_{\text{max}} = 29.5(55) \times 10^3 - 5.4(3) \times 10^5 R^{-3} \quad (4.2)$$

Figure 4.8 (a) Emission spectra of the red form of $\text{Pt}(\text{bpy})\text{Cl}_2$ (**2**) as a function of temperature from 10 to 300 K (adapted from the work of Houlding and Miskowski).⁸
(b) Emission peak energy (ν_{max}) as a function of the inverse cube of the Pt...Pt separation (R^{-3}). Linear fit corresponds to equation 4.2. Error bars are estimated standard deviations.

(a)



(b)



where $\nu_{\max}$ is in cm^{-1} , R is in $\text{\AA}$, and estimated standard deviations are given in parentheses. This linear relationship is reminiscent of the correlation between the emission energy and R^{-3} found for stacked $\text{Pt}(\text{CN})_4^{2-}$ complexes with R values from 3.7 to 3.1 $\text{\AA}$.^{2,42-44} The value of $\nu_{\max}$ as $R \rightarrow \infty$ corresponds to the electronic transition $d\sigma^* \rightarrow \pi^*(\text{bpy})$ in the absence of intercomplex electronic coupling - that is, the transition to the ${}^3\text{MLCT}[d_{z^2}(\text{Pt}) \rightarrow \pi^*(\text{bpy})]$ state in the monomer.⁴⁵ The uncertainty in the predicted ν_{monomer} value is large since the range of measured R values is relatively narrow in this system (3.45-3.37 $\text{\AA}$). Nevertheless, the value for $\text{Pt}(\text{bpy})\text{Cl}_2$ is well below the ν_{monomer} estimates obtained from analysis of the tetracyanoplatinate linear-chain data (36800 cm^{-1} , $\mathbf{E} \perp \mathbf{c}$; 42900 cm^{-1} , $\mathbf{E} \parallel \mathbf{c}$).^{2,46} This difference is not unexpected, since the emissions in these two systems originate from different excited states; in the case of tetracyanoplatinate linear chains, there are two emissive levels, a singlet and a triplet,² and both are predominantly metal-centered $d\sigma^* \rightarrow p\sigma$ states.

The linear relationship between the ${}^3\text{MLCT}$ emission peak position and R^{-3} for $\text{Pt}(\text{bpy})\text{Cl}_2$ is a reflection of the strong dependence of the $d\sigma^*$ energy on metal-metal separation. In the case of stacked $\text{Pt}(\text{CN})_4^{2-}$ units, extended Hückel calculations predict the observed $d\sigma^* \rightarrow p\sigma$ band-gap dependence on R^{-3} .⁴⁷ These calculations,^{44,48} as well as studies of d^8 - d^8 dimers,²⁷ indicate that the energy of the HOMO ($d\sigma^*$) is considerably more sensitive to metal-metal separation than is the energy of the LUMO ($p\sigma$). Indeed, the slope (m) ($-5.4(3) \times 10^5 \text{\AA}^3 \text{cm}^{-1}$) of the fitted line in Figure 47b is slightly less steep than that found for the tetracyanoplatinate linear chains ($-6.3 \times 10^5 \text{\AA}^3 \text{cm}^{-1}$, $\mathbf{E} \perp \mathbf{c}$, triplet; $-8.0 \times 10^5 \text{\AA}^3 \text{cm}^{-1}$, $\mathbf{E} \parallel \mathbf{c}$, singlet).^{2,46} Reported⁷ polarized emission maxima for the red form of $\text{Pt}(\text{bpy})\text{Cl}_2$ at 20 and 298 K also suggest a slightly weaker dependence on metal-metal separation (based on a two-point determination of m : $-5 \times 10^5 \text{\AA}^3 \text{cm}^{-1}$, $\mathbf{E} \perp \mathbf{c}$; $-6 \times 10^5 \text{\AA}^3 \text{cm}^{-1}$, $\mathbf{E} \parallel \mathbf{c}$); similarly, from 10 to 298 K, the lowest-energy feature in the polarized single-crystal absorption spectrum of $\text{Pt}(\text{bpy})\text{Cl}_2$ apparently exhibits a weaker Pt...Pt dependence (two-point determination: $-6 \times 10^5 \text{\AA}^3 \text{cm}^{-1}$, $\mathbf{E} \perp \mathbf{c}$) than found for the

$\text{Pt}(\text{CN})_4^{2-}$ chains ($-8.0 \times 10^5 \text{ \AA}^3 \text{ cm}^{-1}$, $E \perp c$).² It is likely that the R dependence of the $d\sigma^*$ energy is weaker in the $\text{Pt}(\text{bpy})\text{Cl}_2$ chains, owing to the smaller extension of the $d_{z^2}(\text{Pt})$ orbital in the neutral molecule relative to that in the negatively charged $\text{Pt}(\text{CN})_4^{2-}$ complex. It also is possible that the $\text{Pt}(\text{bpy})\text{Cl}_2$ $\pi^*(\text{bpy})$ energy is less sensitive than the $\text{Pt}(\text{CN})_4^{2-}$ $p\sigma$ energy to metal-metal separation.

D. Dependence on Metal-Metal Separation

Given the success of the preceding analysis, it may be surmised that the variations in the spectroscopic properties of compounds **1-9** also are a direct result of the different $\text{Pt}\cdots\text{Pt}$ separations in these materials. Figure 4.9a shows the room-temperature reflectance and emission peak energies as a function of R^{-3} , where R is the $\text{Pt}\cdots\text{Pt}$ separation. In general, these bands shift to lower energy with decreasing $\text{Pt}\cdots\text{Pt}$ separation. Linear fits to these data yield the following expressions for the emission and reflectance band maxima:

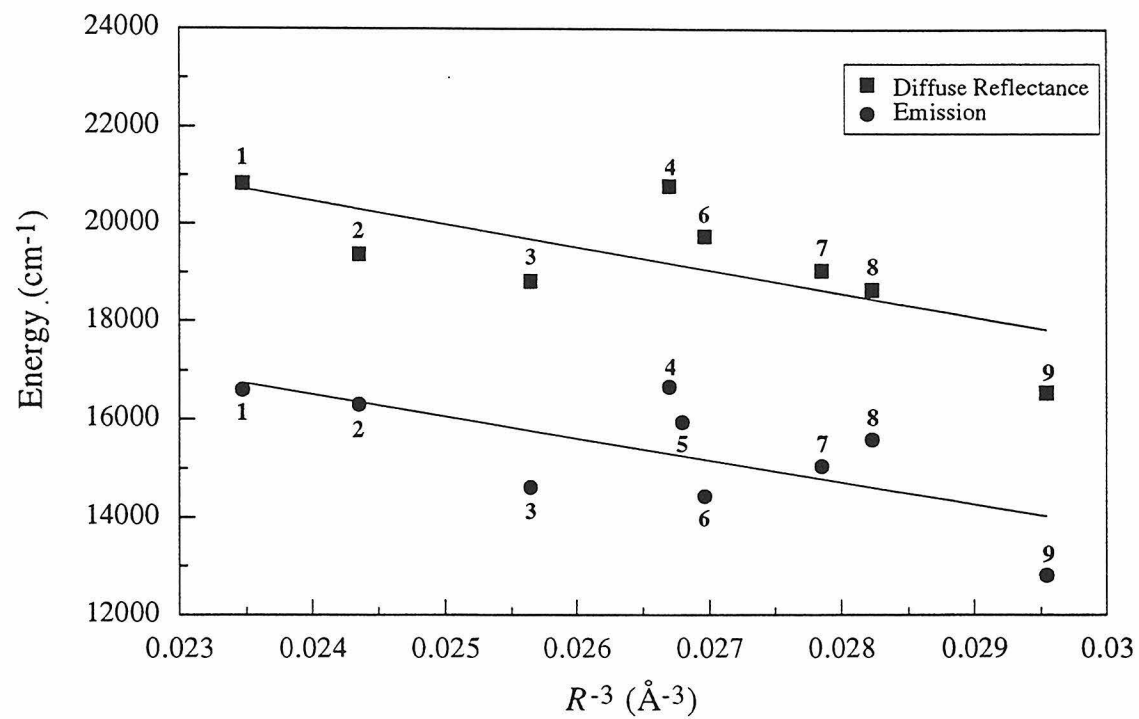
$$\nu_{\text{max}}(\text{emission}) = 27.2 \times 10^3 - 4.5 \times 10^5 R^{-3} \quad (4.3)$$

$$\nu_{\text{max}}(\text{reflectance}) = 31.8 \times 10^3 - 4.7 \times 10^5 R^{-3} \quad (4.4)$$

where ν_{max} is in cm^{-1} , R is in $\text{\AA}$.⁴⁹ The slopes of these fitted lines and the predicted value of ν_{monomer} for emission (given by the intercept in equation 4.3) are slightly less than observed for $\text{Pt}(\text{bpy})\text{Cl}_2$ (equation 4.2). Overall, the correlation between the band maxima and R is not impressive. The data points in Figure 4.9a are much more scattered than observed for $\text{Pt}(\text{bpy})\text{Cl}_2$ and the tetracyanoplatinate salts; in some cases, the deviations from the linear fits are more than 1000 cm^{-1} , far exceeding the experimental uncertainties (typically $<200 \text{ cm}^{-1}$). Moreover, it is not obvious that the peak energies show a strictly linear dependence on R^{-3} , and there is no strong dependence on other structural parameters, such as chain torsion angle.

Figure 4.9 Room-temperature emission and reflectance peak energies of **1-9** plotted as a function of the inverse cube of the Pt...Pt separation (R^{-3}). The linear fits in (a) correspond to equations 4.3-4. Emission data ($\blacklozenge$) for Pt(bpy)Cl₂ (**2**) from 10 to 300 K are shown in (b); the linear fit to these data (solid line) corresponds to equation 4.2. The rectangle outlines the portion of this figure that is plotted in Figure 4.8b. The dashed lines are intended to illustrate, in two cases (*i.e.*, **3** and **4**), the hypothesized relationship between the energies of the MLCT[$d\sigma^* \rightarrow \pi^*$] states and the Pt...Pt separation; these lines *were not* experimentally determined. (The e.s.d.s are typically less than 200 cm⁻¹.)

(a)



(b)

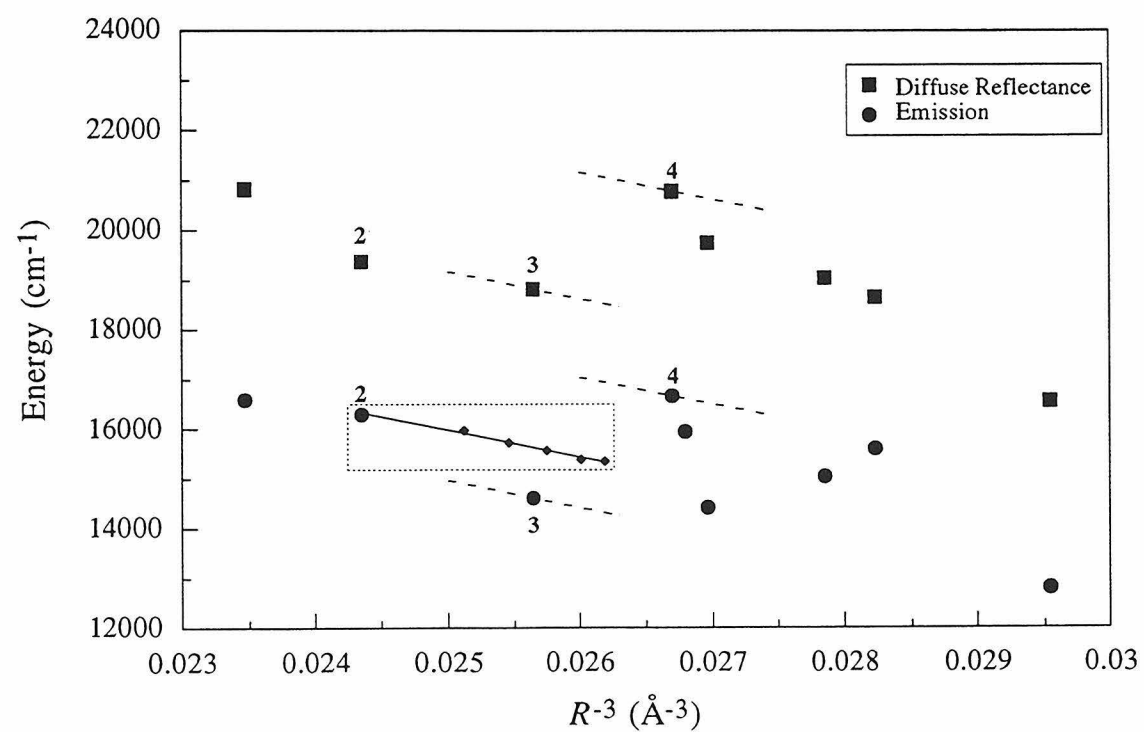
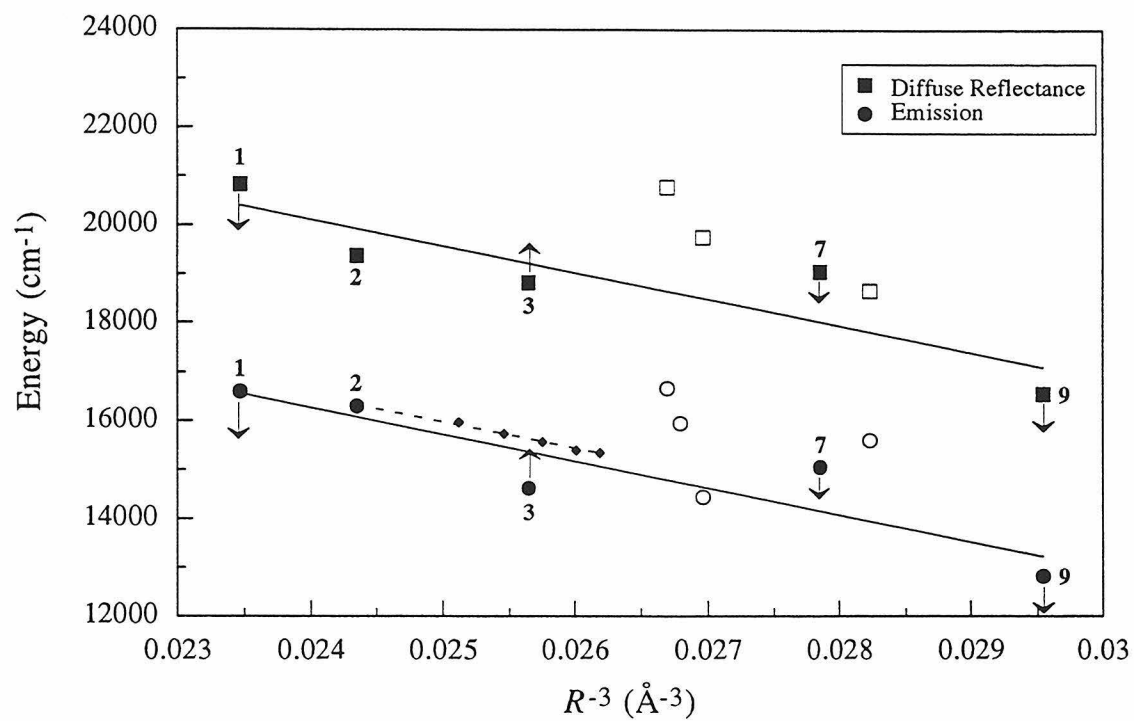
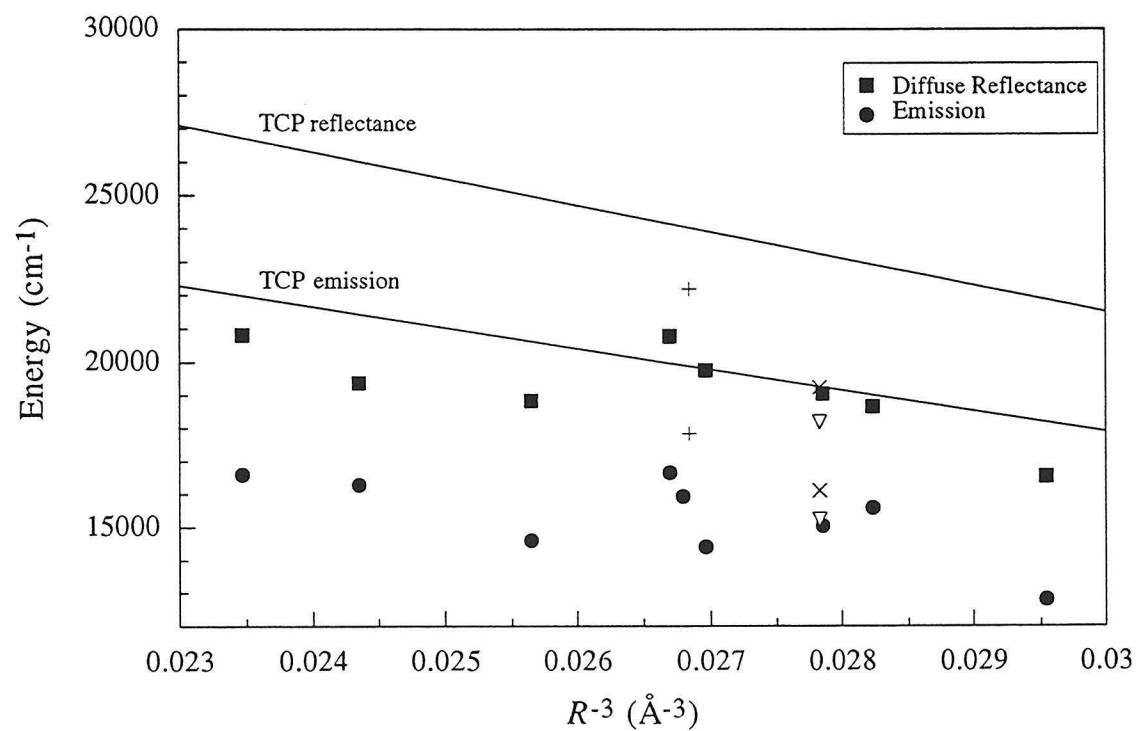


Figure 4.10 Room-temperature emission and reflectance peak energies of **1-9** plotted as a function of the inverse cube of the Pt...Pt separation (R^{-3}). In (a), data for the Pt(diimine)(CN)₂ derivatives are indicated by hollow symbols, and the linear fits (solid lines) determined by the remaining compounds (filled symbols) correspond to equations 4.5-6. Emission data (◆) for Pt(bpy)Cl₂ (**2**) from 10 to 300 K also are shown; the linear fit to these data (dashed line) corresponds to equation 4.2. The arrows indicate the shifts in the MLCT solution absorption band (378-405 nm) with respect to energy of this band in the solution absorption spectrum of Pt(bpy)Cl₂ (**2**). The arrows for the cyanide derivatives (**4**, **5**, **6**, and **8**) are not shown; for the emission data of two of these, the arrowheads would lie below the x axis ($<12000\text{ cm}^{-1}$). In (b), the lines show the empirical linear R^{-3} dependence of the E_{lc} emission and E_{llc} reflectance peak energies for stacked Pt(CN)₄²⁻ complexes (TCP).² Room-temperature emission and reflectance peak energies of [Pt(bpy)(en)][Pt(CN)₄] (+), [Pt(bpy)₂][Pt(CN)₄] (x),¹⁴ and Pt(dmbpy)(ecda) (∇) (ecda = ethyl-2-cyano-3,3'-dimercaptoacrylate);^{50,51} the Pt...Pt distances ($\sim 3.3\text{ Å}$) are less certain for these materials. *It is striking that the emission and reflectance peak energies for all of the platinum(II) diimine linear chains are at lower energy than the corresponding measurements for stacked Pt(CN)₄²⁻ complexes with similar Pt...Pt spacings.*

(a)



(b)



In fact, this result is entirely consistent with our understanding of the electronic structure of compounds **1-9**. In the cases of the tetracyanoplatinate salts² and the thermochromism of Pt(bpy)Cl₂, the Pt...Pt separation is effectively varied while the platinum(II) complexes comprising the chains are unchanged (*e.g.*, Figure 4.8). However, for **1-9** both the Pt...Pt separation *and* the ligands are different for each complex. The impact of the ligands on the electronic structures of these complexes is demonstrated by the solution absorption spectra; the maximum of the ¹MLCT band varies by more than 5000 cm⁻¹ depending on nature of the diimine and the ancillary ligands (Figure 4.3). Thus, the scatter in Figure 4.9a may, to a first approximation, be regarded as a measure of the variations in the properties of these ligands.

Spectroscopic studies of Pt(bpy)Cl₂ and the tetracyanoplatinate salts,² as well as theoretical considerations,^{42,47,48,52} suggest that the optical properties of **1-9** will exhibit a linear dependence on R^{-3} if the ligands surrounding the platinum center remain constant. Therefore, for each of the compounds **1-9** it may be argued that there is a direct relationship between the emission maximum (and diffuse reflectance maximum) and R^{-3} . Dashed lines illustrating this situation are shown in Figure 4.9b for compounds **3** and **4**. The slopes of these lines may deviate from that of the red form of Pt(bpy)Cl₂, since the slope (m) reflects the strength of the intercomplex coupling interactions which may be ligand dependent. On the other hand, the intercepts will almost surely be very different. The value of the intercept ($R \rightarrow \infty$) corresponds to the electronic transition to the ³MLCT[d_{z²}(Pt) → π*(diimine)] state in the monomer - that is, the transition to the dσ* → π*(diimine) state in the absence of intercomplex electronic coupling. The energy of this state will depend strongly on the electronic properties of the surrounding ligands.⁵³

Within this framework, the scatter in Figure 4.9a results from differences in intercomplex coupling within the chains, as well as differences in the d_{z²}-π* energy gaps of the corresponding monomers. (Even variations in the Franck-Condon factors that

determine emission bandshape may be cast in terms of these parameters.) Clearly, further studies are necessary to elucidate their relative importance. However, the fact that m for $\text{Pt}(\text{bpy})\text{Cl}_2$ is similar to - only ~15% smaller than - that found for the tetracyanoplatinate salts, suggests that the ligand variations in **1-9** do not lead to vastly different electronic coupling. If the coupling interactions in **1-9** are similar, the emission maxima for these compounds are expected to exhibit a linear dependence on R^{-3} with approximately the same slope as observed for $\text{Pt}(\text{bpy})\text{Cl}_2$ ($m = -5.4(3) \times 10^5 \text{ \AA}^3 \text{ cm}^{-1}$).⁵³ With this value of m , we can provide estimates of the changes in Pt...Pt separation at low temperature for compounds **1-9** from the red-shift in their emission maxima at lower temperature. These values, along with estimated coefficients of linear thermal expansion along the chain axis at room temperature (α),⁵⁴ are listed in Table 4.2.⁵⁵

Table 4.2. Estimated shrinkage of the Pt...Pt separation ($-\Delta$) at low temperature, and corresponding coefficient of linear thermal expansion at room temperature (α)⁵⁴ along the chain axis.

Compound	Temperature Range	$-\Delta(\text{Pt}\cdots\text{Pt})$, $\text{\AA}$	α , 10^5 K^{-1}
$\text{Pt}(\text{dmbpy})(\text{NCO})_2$ (1)	295 $\rightarrow$ 10 K	0.01	1
$\text{Pt}(\text{bpy})\text{Cl}_2$ (2)	295 $\rightarrow$ 10 K	0.08	9.4(3)
$\text{Pt}(\text{bpy})(\text{CN})_2$ (4)	295 $\rightarrow$ 30 K	0.10	11
$\text{Pt}(\text{phen})(\text{CN})_2$ (6)	295 $\rightarrow$ 30 K	0.09	10
	295 $\rightarrow$ 30 K	0.13 ($\mathbf{E} \perp \mathbf{c}$; $\mathbf{E} \parallel \mathbf{c}$)	15
$\text{Pt}(\text{bpy})(\text{NCS})_2$ (7)	295 $\rightarrow$ 10 K	0.04	4
$\text{Pt}(\text{bpm})(\text{CN})_2 \cdot \text{dmf}$ (8)	295 $\rightarrow$ 30 K	0.07 ($\mathbf{E} \perp \mathbf{c}$)	8
	295 $\rightarrow$ 30 K	0.09 ($\mathbf{E} \parallel \mathbf{c}$)	10
$\text{Pt}(\text{bpy})(\text{NCO})_2$ (9)	295 $\rightarrow$ 10 K	0.05	5

^a The values given for $\text{Pt}(\text{bpy})\text{Cl}_2$ (**2**) were determined from the variable temperature study of the crystal structure.

The values in Table 4.2 are only crude estimates because this analysis is fraught with assumptions (estimated uncertainty, 30%).⁵⁶ Nevertheless, it is apparent that the magnitude of the coefficients of linear thermal expansion are quite reasonable for platinum(II) chain structures;² thus, the assumption of approximately equal intercomplex coupling interactions for **1-9** is not invalidated by this analysis. These results indicate that the red-shift in the emission maxima with decreasing temperature for compounds **1-9** is entirely consistent with a shrinkage of the Pt...Pt separation with decreasing temperature. Interestingly, the Pt...Pt separation in Pt(dmbpy)(NCO)₂ is relatively insensitive to temperature; it is possible that the methyl groups of the bipyridyl ligand inhibit compression of the chain. In contrast, the dicyano complexes, **4**, **6** and **8**, are predicted to show the largest values of α for this series of compounds; therefore, these materials are ideal candidates for low temperature structural studies. In the case of Pt(phen)(CN)₂ (**6**), the emission maximum exhibits a linear dependence on hydrostatic pressure ($-70\text{ cm}^{-1}/\text{kbar}$) over the 1-30 kbar range (total shift, -2000 cm^{-1}).²⁴ Thus, we predict that the Pt...Pt separation decreases by a total of $0.14\text{ \AA}$ in this experiment, corresponding to $0.0049\text{ \AA/kbar}$. The corresponding linear compressibility ($1.5 \times 10^{-3}\text{ kbar}^{-1}$, 295 K, 1 bar) is somewhat smaller than found for stacked tetracyanoplatinate complexes ($3\text{-}5 \times 10^{-3}\text{ kbar}^{-1}$); we would have calculated a larger value if we had assumed weaker coupling (more positive m) than was found for **2**.

The solution absorption spectra of **1-9** (Figure 4.3a) indicate that cyanide ligands strongly perturb the electronic structures of these complexes. For example, in the dicyanide complexes the lowest observed ¹MLCT transition is shifted by more than 4000 cm^{-1} to higher energy of the lowest MLCT band in the spectrum of Pt(bpy)Cl₂. For the remaining five complexes, variations in the energy of this band are more modest (405-368 nm; 2500 cm^{-1}) since the electronic properties of these ligands (SCN⁻, OCN⁻, Cl⁻) are more similar to each other than to cyanide. Consequently, the plot of solid-state emission and reflectance band maxima as a function of R^{-3} in Figure 4.10a distinguishes

between the cyanide derivatives and the remaining complexes. A linear fit to the room-temperature emission data (*excluding* the four dicyanide complexes) shows remarkable (though perhaps fortuitous) agreement with the fit obtained from the variable temperature study of Pt(bpy)Cl₂ (equation 4.2):

$$\nu_{\max}(\text{emission}) = 29.6 \times 10^3 - 5.5 \times 10^5 R^{-3} \quad (4.5)$$

$$\nu_{\max}(\text{reflectance}) = 33.6 \times 10^3 - 5.8 \times 10^5 R^{-3} \quad (4.6)$$

where $\nu_{\max}$ is in cm⁻¹, R is in Å.⁴⁹ Interestingly, the emission maximum for Pt(bpm)Cl₂ (**3**) lies 1000 cm⁻¹ below the value predicted from the linear fit derived for Pt(bpy)Cl₂ (equation 4.2); similarly, the emission maximum for Pt(bpy)(NCS)₂ (**7**) lies 600 cm⁻¹ to higher energy of the predicted value. It is striking that the lowest-energy ¹MLCT features in the solution absorption spectra of **3** and **7** also are shifted by -800 and +600 cm⁻¹, respectively, from the maximum of this band in the spectrum of Pt(bpy)Cl₂. The shifts in the positions of the solution MLCT band are indicated with arrows in Figure 4.10a. In the cases of the cyanate (**1** and **9**) and cyanide derivatives (**4**, **5**, **6**, and **8**), the shifts in the solution absorption band do not match the deviations from the values predicted using equation 4.2; this is particularly pronounced for the cyanide derivatives with MLCT shifts >4000 cm⁻¹ (not shown in Figure 4.10a). However, the weak correlation between the solution absorption band and the relative energies of the ³MLCT[dσ*→π*] states in **1-9** is not unexpected, since the solution absorption band corresponds to a transition to a ¹MLCT[dπ→π*] state. Ligand field theory predicts that the energies of the dπ and d_{z2} levels exhibit different dependencies on the electronic properties of the ligands. Notably, as suggested by the dicyano data, the dπ levels are more stabilized by the cyanide ligands than is the dσ*(d_{z2}) level. In fact, it appears that the strong σ-donation (energy raising) and π-accepting (energy lowering) effects of CN⁻ ligands on the energy of the dσ* level nearly offset each other, thus accounting for the

somewhat surprising clustering of the cyanide data points near those of the other compounds in Figures 4.9-10.

At this juncture, the variations in energy of the MLCT[$d\pi \rightarrow \pi^*$] states cannot be quantitatively explained. However, several trends emerge from our analysis of these data. In equations 4.2-6, the value of $\nu_{\max}$ as $R \rightarrow \infty$ corresponds to the electronic transition $d\sigma^* \rightarrow \pi^*$ (diimine) in the absence of intercomplex electronic coupling - that is, the transitions to the singlet (diffuse reflectance) or triplet (emission) MLCT[$d_{z^2}(\text{Pt}) \rightarrow \pi^*$] states. As found for $\text{Pt}(\text{bpy})\text{Cl}_2$ ($29.5(55) \times 10^3$), the predicted ν_{monomer} values are well below estimates obtained for stacked $\text{Pt}(\text{CN})_4^{2-}$ units with R values from 3.7 to 3.1 Å (emission: 36800 cm^{-1} , $\mathbf{E} \perp \mathbf{c}$; 42900 cm^{-1} , $\mathbf{E} \parallel \mathbf{c}$; reflectance: 45.5 cm^{-1} , $\mathbf{E} \parallel \mathbf{c}$; absorption: 43900 cm^{-1} , $\mathbf{E} \perp \mathbf{c}$).² (For comparison, Figure 4.10b shows the empirical linear R^{-3} dependence of the $\mathbf{E} \perp \mathbf{c}$ emission and $\mathbf{E} \parallel \mathbf{c}$ reflectance peak energies for stacked $\text{Pt}(\text{CN})_4^{2-}$ complexes.) This result is expected since the values of ν_{monomer} determined for the tetracyanoplatinate linear chains correspond to different excited states - namely the predominantly metal-centered singlet and triplet $d\sigma^* \rightarrow p\sigma$ states (Figure 4.1). Unfortunately, the assignment of the transitions to the monomer singlet and triplet MLCT[$d_{z^2}(\text{Pt}) \rightarrow \pi^*(\text{bpy})$] states in the solution absorption spectra of 1-9 is complicated by the presence of intense charge-transfer features. However, it is satisfying that the estimated energies for this state are higher than the energies of the lowest $^1\text{MLCT}$ absorption bands (Figure 4.3) as expected for the ordering of d-orbitals in a PtN_2X_2 complex ($z^2 < xz, yz$).⁵⁷ The dependence of the energies of the $d\sigma^* \rightarrow \pi^*$ states, given by the slopes in equations 4.2-6, also is slightly weaker than observed for $d\sigma^* \rightarrow p\sigma$ states of stacked $\text{Pt}(\text{CN})_4^{2-}$ complexes. This result may be attributed, in part, to the smaller extension of the $d_{z^2}(\text{Pt})$ orbital in the neutral molecules, as well as a weaker dependence of the energy of the π^* LUMO on $\text{Pt} \cdots \text{Pt}$ separation.

The solid-state emission and reflectance measurements for the $[\text{Pt}(\text{bpy})(\text{en})][\text{Pt}(\text{CN})_4]$ and $[\text{Pt}(\text{bpy})_2][\text{Pt}(\text{CN})_4]$ double salts,¹⁴ as well as the neutral

Pt(dmbpy)(ecda) (ecda = ethyl-2-cyano-3,3'-dimercaptoacrylate) complex, also are shown in Figure 4.10b;^{50,51} the Pt...Pt distances (~ 3.3 Å) are less certain for these materials. The data for Pt(dmbpy)(ecda) lie within the range of scatter found for **1-9**, indicating a similar origin for these spectroscopic features. We also have observed a well-resolved shoulder near 493 nm (20300 cm^{-1}) in the reflectance spectrum for the orange form of Pt(phen)(NCS)₂;⁵⁸ from the general dependence of the reflectance maximum on Pt...Pt distance, this energy is consistent with a stacked structure having metal-metal spacings of ~ 3.4 Å. For [Pt(bpy)₂][Pt(CN)₄], the emission and reflectance maxima fall within the range observed for **1-9**, while the maxima for [Pt(bpy)(en)][Pt(CN)₄] are somewhat higher in energy. These differences may be attributable, in part, to the different ligands in these systems, as well as somewhat different solid-state structures. In both cases, the band energies are still lower than observed for tetracyanoplatinate salts with comparable Pt...Pt spacings (Table 4.3). The spectroscopy of the double salts suggests that these materials are electronically similar to the neutral linear-chain solids.¹⁴ However, further structural information on these materials is sorely needed.

E. On The Nature of the Linear-Chain MLCT State

Our interpretation of the spectroscopy and photophysics of platinum(II) diimine linear-chain complexes differs from that offered by Gliemann and co-workers^{7,16,23,24,59,60} – though many aspects of these descriptions are not mutually incompatible. The chief distinction is the assignment of the lowest energy spin-allowed and spin-forbidden transitions. As indicated in Figure 4.1, these are the transitions to the singlet and triplet MLCT[$d\sigma^*(\text{Pt}) \rightarrow \pi^*(\text{diimine})$] states where the LUMO is the predominantly ligand-localized π^* orbital. In contrast, Gliemann and co-workers emphasize the p_z and $\pi^*(\text{CN})$ character of the LUMO for Pt(bpy)(CN)₂ (**4**),²³ Pt(phen)(CN)₂ (**6**),²⁴ and Pt(bpm)(CN)₂·dmf (**8**).^{16,59,60} There is a close analogy

between this interpretation and that given for the spectroscopy of stacked $\text{Pt}(\text{CN})_4^{2-}$ complexes whose lowest-energy states are the predominantly metal-centered $d\sigma^* \rightarrow p\sigma$ states, where the $p\sigma$ level has partial $\pi^*(\text{CN})$ character.²

Generally, MLCT transitions involving diimine ligands occur at lower energy than those involving cyanide.⁶¹ For example, the lowest spin-allowed MLCT bands in the solution absorption spectra of $\text{Pt}(\text{diimine})(\text{CN})_2$, $\text{Pt}(\text{bpy})_2^{2+}$, and $\text{Pt}(\text{bpy})(\text{en})^{2+}$ complexes originate near 30000 cm^{-1} , whereas the lowest (predominantly singlet) MLCT transition for $\text{Pt}(\text{CN})_4^{2-}$ occurs near 38000 cm^{-1} .⁶² Moreover, the vibronic sidebands ($1400\text{--}1500\text{ cm}^{-1}$) in the low-temperature emission spectra of $\text{Pt}(\text{bpy})\text{Cl}_2$ (**2**), $\text{Pt}(\text{bpy})(\text{CN})_2$ (**4**) and $\text{Pt}(\text{bpm})(\text{CN})_2 \cdot \text{dmf}$ (**8**) are diagnostic^{63,64} of the involvement of the bipyridyl ligand in the electronic transition.^{9,14} Similar structure is evident in the single-crystal polarized emission and absorption spectra;^{7,16,23,24} thus, in the cases of **2**, **4** and **8**, there is a mirror-image relationship between the structured, spin-forbidden absorption and phosphorescence spectra ($E \perp c$). A telling comparison exists between the lowest MLCT [$d\sigma^* \rightarrow \pi^*$] states of the Pt diimine chains and the $d\sigma^* \rightarrow p\sigma$ states of the tetracyanoplatinate salts. Qualitatively, the differences are obvious; the diimine complexes always absorb at lower energies than $\text{Pt}(\text{CN})_4^{2-}$ salts with similar Pt...Pt spacings (Table 4.3; Figure 4.10b). The room-temperature emission maxima for **1-9** also are shifted by $3500\text{--}6000\text{ cm}^{-1}$ to lower energy of the emission from tetracyanoplatinate salts. Similarly, our estimates for the energies of the singlet and triplet $d_{z^2} \rightarrow \pi^*(\text{diimine})$ states of the corresponding monomers of **1-9** (ν_{monomer} from equations 4.2-6) also are consistently lower than those for the $d_{z^2} \rightarrow p_z/\pi^*(\text{CN}^-)$ transitions in $\text{Pt}(\text{CN})_4^{2-}$.^{2,62} In the case of stacked $\text{Pt}(\text{en})\text{Cl}_2$ complexes (Pt...Pt $3.38\text{ \AA}$), the intense $E \parallel c$ polarized transition to the singlet $d\sigma^* \rightarrow p\sigma$ state (285 nm) is strongly blue-shifted (16000 cm^{-1}) with respect to the transition to the singlet $d\sigma^* \rightarrow \pi^*$ state (531 nm) measured in the diffuse reflectance spectrum of $\text{Pt}(\text{bpm})\text{Cl}_2 \cdot \text{nmp}$ (**3**). We conclude that, while mixing of the $\pi^*(\text{diimine})$ level with the $p\sigma(\text{Pt})$ and $\pi^*(\text{CN})$ levels is symmetry allowed and surely occurs to some

extent, the LUMOs for **1-9** are reasonably well-described as the predominantly ligand-centered π^* orbital of the diimine (Figure 4.1).

Table 4.3. Emission maxima for linear-chain platinum(II) diimine complexes and tetracyanoplatinate salts² with similar Pt...Pt separations.

Platinum(II) Diimine Chains				Tetracyanoplatinate Chains ²	
Compound	Emission, cm ⁻¹	Pt...Pt, Å	Pt...Pt, Å	Emission, cm ⁻¹	Compound
Pt(dmbpy)(NCO) ₂ (1) (orange)	16650	3.49	3.48	21900	K ₂ [Pt(CN) ₄]·3H ₂ O (light-yellow)
Pt(bpy)Cl ₂ (2) (red)	16300	3.45	3.42	21100	Rb ₂ [Pt(CN) ₄]·1.5H ₂ O (pale green)
Pt(bpy)(CN) ₂ (4) (orange)	16670	3.35	3.36	20200	Mg[Pt(CN) ₄]·4.5H ₂ O (yellow-green)
Pt(bpy)(NCS) ₂ (7) (red)	15050	3.30	3.32	19500	Ba[Pt(CN) ₄]·4H ₂ O (yellow-green)
Pt(bpy)(NCO) ₂ (9) (blue)	12800	3.24	3.25	18550	Sr[Pt(CN) ₄]·2H ₂ O (orange)
—	—	—	3.18	16800	Tb ₂ [Pt(CN) ₄] ₃ ·21H ₂ O (red)

The electronic structural model proposed by Gliemann and co-workers^{7,16,23,24} is couched in the language of solid-state spectroscopy (which has been reviewed elsewhere)^{65,66} and closely parallels the model proposed for stacked Pt(CN)₄²⁻ complexes.² The lowest-energy spin-allowed (**E**||**c**) and spin-forbidden (**E**⊥**c**) absorption bands are assigned to transitions to the singlet and triplet components of the $d\sigma^* \rightarrow \text{LUMO}$ delocalized free-exciton (FE) states. The phosphorescence (**E**⊥**c**) is proposed to originate from the corresponding lower-energy triplet self-trapped exciton (STE) states; these excitons can migrate by a phonon-assisted hopping mechanism.⁶⁷ The fluorescence (**E**||**c**) has been attributed to emission from either the singlet FE or STE states;^{7,16} there is evidently some confusion surrounding this assignment. In short, these authors propose four types of low-lying excited states corresponding to the singlet and

triplet $d\sigma^* \rightarrow \text{LUMO}$ FE and STE states. In contrast, our MO picture provides for two types of low-lying excited states corresponding to the singlet and triplet $d\sigma^* \rightarrow \pi^*$ states (Figure 4.1).

In the case of the platinum(II) diimine linear-chains, there is no direct evidence that distinguishes between these FE and STE states. It is apparent that the motivation for proposing this model is the close analogy to the literature describing the electronic structure of the tetracyanoplatinate salts where the FE/STE description is deeply entrenched.² The MO description is readily expanded to include both localized and delocalized excited states; in that case, the model converges on that proposed by Gliemann with the exception of a somewhat different LUMO. However, in the absence of experimental data distinguishing these four types of low-lying excited states, we do not introduce this complication. As we and others have established,¹⁴ the spectroscopy of these platinum(II) diimine linear-chains, including the extensive single-crystal measurements of Gliemann and co-workers,^{7,16,23,24} is readily interpreted within the framework of the MO model describing the $d\sigma^* \rightarrow \pi^*$ excited states.⁶⁸

Studies of tetracyanoplatinate linear chains indicate that the triplet excitation is rather localized in these systems.⁶⁷ We envision a similar situation for the platinum(II) diimine chains, involving an excited-state delocalized over a few stacked complexes. Indeed, the fact that the Stokes shift between the diffuse reflectance and emission maxima ($\sim 4000 \text{ cm}^{-1}$) is similar to that observed for stacked $\text{Pt}(\text{CN})_4^{2-}$ complexes ($3500\text{--}4700 \text{ cm}^{-1}$; E_{lc} reflectance - E_{lc} emission; $\text{Pt}\cdots\text{Pt}$, $3.2\text{--}3.5 \text{ \AA}$)² suggests that the $d\sigma^* \rightarrow p\sigma$ and $d\sigma^* \rightarrow \pi^*$ states have comparable singlet-triplet splittings of $1000\text{--}2000 \text{ cm}^{-1}$. This gap is smaller than those found for $d\sigma^* \rightarrow p\sigma$ states of binuclear d^8 complexes ($\sim 5000 \text{ cm}^{-1}$)^{25,27,28} and the unimolecular MLCT states of platinum(II) diimine complexes ($3000\text{--}4000 \text{ cm}^{-1}$; see Chapter 1);⁹ this result is consistent with the somewhat more delocalized nature of $d\sigma^* \rightarrow \pi^*$ excitation. In analogy to d^8 binuclear complexes, formation of a $d\sigma^* \rightarrow \pi^*$ excited state should lead to significant distortion along the chain

axis. Depopulation of the Pt...Pt antibonding $d\sigma^*$ level is expected to induce shortening of the metal-metal separation. In the case of $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4+}$, a 7% shrinkage of the Pt...Pt bond was inferred from a Franck-Condon analysis of the emission spectrum;²⁸ one interpretation of excited-state XAFS (X-ray absorption fine-structure) data suggests an even larger excited-state distortion (18% shrinkage).⁶⁹ For linear-chains, the magnitude of this distortion for a single Pt...Pt contact is expected to be related to the degree of excitation delocalization; more delocalized excited-states will lead to smaller changes in individual Pt...Pt distances. In this context, it is intriguing that the emission profile for $\text{Pt}(\text{dmbpy})(\text{NCO})_2$ (**1**) is somewhat broader than observed for **2-9** (Figures 4.4-5). The weak temperature dependence of the emission maximum may indicate a steeper deformation potential for compression along the chain axis, which, in principle, could lead to a more delocalized excitation and a broadened emission spectrum.

The profiles of the $^3\text{MLCT}[d\sigma^* \rightarrow \pi^*]$ emission for the linear-chain platinum(II) diimine complexes are characteristically narrow with similar Franck-Condon factors. The Huang-Rys ratios ($S, I_{1,0}/I_{0,0}$), characterized by the diimine vibronic structure, are typically 0.2-0.5, with the platinum(II) diimine double salts having the larger values of S (~ 0.5) than the neutral complexes.¹⁴ In contrast, S is typically 1-1.3 for unimolecular MLCT and $\pi \rightarrow \pi^*$ emission. Thus, the Franck-Condon factors appear to be a useful means of distinguishing between these excited states.^{9,14} The larger Franck-Condon factors associated with the unimolecular MLCT suggest an increased diimine excited-state distortion. This is consistent with a MLCT state involving a π -bonding $d\pi(xz, yz)$ level. The distortion may be smaller for the $^3\text{MLCT}[d\sigma^* \rightarrow \pi^*]$ excited-state because the $d\sigma^*$ level is formally π -nonbonding to the diimine. Similar arguments, invoking changes in $d\pi$ -backbonding, have been advanced to account for wide variations in S for the emissions from Ru(II) and Os(II) bipyridyl complexes.⁷⁰ Additionally, increased π^* - $p\sigma$ mixing in the linear-chain complexes with respect to π^* - p_z mixing in the monomers also will tend to reduce S .⁷¹

It is evident that the triplet excitation also is mobile - presumably diffusing more rapidly along the chains than between chains. We have observed a laser power dependence for the emission from $\text{Pt}(\text{bpy})(\text{NCO})_2$ (**9**) ($\text{Pt}\cdots\text{Pt}$ 3.24 Å); the non-linear increase in emission intensity with increasing laser power is attributable to triplet-triplet excited-state quenching. Miskowski and Houlding^{8,14} have observed very strong quenching of the emission from Ni-doped samples of $[\text{Pt}(\text{bpy})_2][\text{Pt}(\text{CN})_4]$, indicating that the excitation travels between 50-100 repeat units (300-600 Å) during its 8 ns lifetime; similar results have been obtained for the stacked $\text{Pt}(\text{CN})_4^{2-}$ complexes.⁷² Obviously, the issues of excitation mobility and directionality are of fundamental importance for photochemical, photovoltaic and electro-optical applications. At this juncture, however, little is known about excitation mobility in the stacked platinum(II) diimine systems, and further work is required.

The possibility of switching between lowest excited states in a material by a small perturbation (*e.g.*, temperature, pressure, electric field) is of both practical and theoretical interest. The emission spectroscopy of these linear-chain materials suggests that as the $\text{Pt}\cdots\text{Pt}$ separation increases, the energy of the $^3\text{MLCT}[\text{d}\sigma^*(\text{Pt})\rightarrow\pi^*(\text{diimine})]$ state will at some distance surpass the energies of the lowest monomer excited states (*e.g.*, $^3\pi\rightarrow\pi^*$, $^3\text{d}\rightarrow\text{d}^*$, and $^3\text{MLCT}$ states). For $\text{Pt}\cdots\text{Pt}$ separations longer than this crossover distance, the emission will originate from a lowest unimolecular excited state. This crossover distance is dependent on the energy of the lowest monomer excited state. For example, the 0-0 energy of the lowest $^3\text{d-d}$ state for the yellow form of $\text{Pt}(\text{bpy})\text{Cl}_2$ is near 500 nm (see Chapter 2), whereas the emission for **2** ($\text{Pt}\cdots\text{Pt}$ 3.45 Å) originates near 550 nm at room temperature. In contrast, the 0-0 energy of the lowest $^3\pi\rightarrow\pi^*$ state for the yellow form of $\text{Pt}(\text{dmbpy})(\text{NCO})_2$ is near 460 nm, whereas the emission for **1** ($\text{Pt}\cdots\text{Pt}$ 3.49 Å) originates near 510 nm at room temperature. From the dependence of the emission from $\text{Pt}(\text{bpy})\text{Cl}_2$ (**2**) on $\text{Pt}\cdots\text{Pt}$ separation (equation 4.2), the estimated monomer-chain emission crossover distances are 3.7 and 3.6 Å for **1** and **2**, respectively. For

Pt(bpm)(CN)₂·dmf (**8**), crossover is estimated to occur near 3.45 Å which is somewhat longer than the Pt···Pt separation in crystals containing dimers, such as Pt(bpm)(CN)₂ (3.44 and 3.27 Å)⁵⁹ and Pt(bpm(CN)₂·H₂O (Pt···Pt 3.49 Å);⁶⁰ the fact that these dimers exhibit ³π→π* intraligand emission is not unexpected since the metal-metal interactions are effectively halved relative to the chain structure.

Similarly, since the dσ*-pσ gap is slightly more sensitive to metal-metal separation than the dσ*-π* gap, we anticipate that at some very short Pt···Pt spacing, the dσ*→pσ lowest triplet will lie lower than the dσ*→π* states. Based on the linear dependence on R^{-3} of the ELc emission from the dσ*→pσ states of the tetracyanoplatinate salts, a coarse estimate for the dσ*→pσ/dσ*→π* crossover for Pt(bpy)Cl₂ (**2**) is 2.8 Å.⁷³ While the validity of using the tetracyanoplatinate dσ*→pσ energy to predict the energy of this state in the platinum(II) diimine chains is admittedly suspect, the absence of experimental values leaves us with few options. We expect that the crossover will occur at a Pt···Pt separation less than 3.0 Å. Even under high pressure, it seems unlikely that this distance can be approached using compounds **1-9**, and in all probability, novel platinum(II) diimine chain materials will be necessary to experimentally observe this crossover.

IV. Conclusion

Crystals composed of stacked platinum(II) diimine complexes with short metal-metal separations (<3.5 Å) are more intensely colored than their monomer constituents. This study demonstrates that the spectroscopy of these materials is readily described using a molecular orbital model which considers the electronic interactions between adjacent platinum centers. In this scheme, the colors of these solids are attributed to an electronic transition to the ¹MLCT[dσ*(Pt)→π*(diimine)] state, where the dσ* level derives from the interaction of the Pt 5d₂₂ orbitals of adjacent complexes. The emission from these materials originates from the corresponding triplet MLCT[dσ*→π*] state.

We emphasize that the LUMO is clearly the predominantly ligand-centered π^* orbital of the diimine; this situation differs from that of stacked $\text{Pt}(\text{CN})_4^{2-}$ complexes and some binuclear d^8 complexes where the $d\sigma^* \rightarrow p\sigma$ states are lowest in energy. Thus, modification of the ligands surrounding the platinum center is a potentially powerful tool for tuning the properties of these materials.

This electronic structural model also accounts for the red-shift in these transitions with decreasing Pt...Pt separation; enhanced $5d_{z^2} \cdots 5d_{z^2}$ interaction stabilizes the MLCT[$d\sigma^* \rightarrow \pi^*$] levels. In the case of the red form of $\text{Pt}(\text{bpy})\text{Cl}_2$, the emission peak energy shifts to lower energy by $\sim 950 \text{ cm}^{-1}$ when the temperature is decreased from 300 to 10 K; over this temperature range, the Pt...Pt separation shrinks by 0.08 Å. We find that for $\text{Pt}(\text{bpy})\text{Cl}_2$, the emission peak energies exhibit a linear dependence on the inverse cube of the Pt...Pt separation (R^{-3}). The fact that this relationship differs somewhat from that observed for tetracyanoplatinate linear chains is entirely consistent with our understanding that the emissions in these two systems originate from different electronic states. Our spectroscopic measurements for a series of linear-chain compounds with different diimine and ancillary ligands indicate that the emission and lowest diffuse reflectance peak energies do not follow the same R^{-3} dependence that was observed for $\text{Pt}(\text{bpy})\text{Cl}_2$. This result is readily understood in terms of the different electronic properties of the ligands surrounding the platinum centers, emphasizing the impact of the ligands on the electronic structure of these materials.

V. References and Notes

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- (29) Recently Kato and co-workers²⁰ have examined the spectroscopy of Pt(*i*-biq)(CN)₂·H₂O (**5**) (*i*-biq=3,3'-biisoquinoline), Pt··Pt 3.34 Å. The unstructured

emission ($\lambda_{\text{max}}=627$ nm) room-temperature originates from a lowest $^3\text{MLCT}[\text{d}_{z^2}(\text{Pt})\rightarrow\pi^*(\text{bpy})]$ state. We cannot estimate the linear coefficient of thermal expansion (α) from the low temperature spectrum since the band profile is evidently complicated by $\pi\rightarrow\pi^*$ excimer emission. (In 77 K frozen solutions, the emission clearly originates from a lowest ligand-localized $^3\pi\rightarrow\pi^*$ state.) We also are unable to identify a $^1\text{MLCT}$ transition in the solution absorption spectra because of intense, overlapping intraligand transitions for $\lambda<380$ nm.

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- (32) The room-temperature emission maximum for $\text{Pt}(\text{phen})(\text{CN})_2$ (**6**) has been previously reported at 691¹⁴ and 715 nm;⁸ the $\text{E}_{\perp\text{c}}$ emission maximum was observed at 660 nm.²⁴ We find the maximum at 693 nm in our spectra, and we have adopted that value here, though there is clearly disagreement surrounding this result.
- (33) The rising baseline in the diffuse reflectance spectrum of $\text{Pt}(\text{bpm})(\text{CN})_2\cdot\text{dmf}$ (**8**) is an experimental artifact. The sample was supported in a MgSO_4/dmf slurry in order to avoid formation of surface hydrate.
- (34) Crystals of **9** are too strongly absorbing for a qualitative assessment of dichroism.
- (35) In reference 7, the reported ϵ ($2500\text{ M}^{-1}\text{cm}^{-1}$, 521 nm) for the $\text{d}\sigma^*\rightarrow\pi^*$ band in the $\text{E}_{\perp\text{c}}$ single-crystal absorption spectrum of $\text{Pt}(\text{bpy})\text{Cl}_2$ (**2**) implies an absorbance of ~ 15.2 for the $10\text{ }\mu\text{m}$ thick sample used in their study; though this value is reported twice in this manuscript, we believe $250\text{ M}^{-1}\text{cm}^{-1}$ to be a more reasonable estimate. In the case of $\text{Pt}(\text{phen})(\text{CN})_2$ (**6**),²⁴ using the density (2.38 g/cm^3) calculated from the crystal structure, the extinction coefficient for the $\text{E}_{\perp\text{c}}$ single-crystal absorption maximum is estimated to be 75 (526 nm) at 298 K and $170\text{ M}^{-1}\text{cm}^{-1}$ (568 nm) at 6 K .
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- (38) Miskowski and Houlding⁸ have noted that, at least in the case of $\text{Pt}(\text{bpy})(\text{CN})_2$, there is disagreement in the measured room-temperature-emission lifetimes reported by various groups.^{15,23} However, since the emission profiles are very reproducible in several laboratories, it appears that the emissions are intrinsic to these linear-chain materials. The variability in the emission lifetimes reflects the complexity of the nonradiative decay processes whose rates may be strongly influenced by sample preparation and history.

- (39) We have not extensively investigated the fluorescence (**Elle**) that has been reported by Gliemann's group.^{7,16,23,24} It is clear that any sub-nanosecond emission components make no significant contribution to the steady-state emission spectra we have recorded.
- (40) The emissive state in the yellow form of Pt(bpy)Cl₂ is clearly a ³d→d state (Chapter 2). In contrast, for Pt(bpm)Cl₂ in EMD 77 K glassy solution, we observed a structured emission ($\Delta\nu \sim 1100 \text{ cm}^{-1}$) originating near 450 nm, indicating a lowest ³ $\pi \rightarrow \pi^*$ state. The electronic structure is an intriguing question because the lowest MLCT and intraligand states must be nearly degenerate. While these observations are not inconsistent with the relative ligand field strengths of the diimine ligands, a luminescent impurity cannot be ruled out without further investigation.
- (41) Values of *R* at 10 and 300 K were obtained from extrapolation of equation (4.1); as the coefficient of thermal expansion is expected to decrease at low temperature, the Pt...Pt separation at 10 K may be somewhat underestimated.
- (42) Day, P. *J. Am. Chem. Soc.* **1975**, 97, 1588.
- (43) Yersin, H.; Gliemann, G. *Ber. Bunsenges. Phys. Chem.* **1975**, 79, 1050.
- (44) Yersin, H.; Gliemann, G.; Rössler, U. *Solid State Comm.* **1977**, 21, 915.
- (45) The assignment of the monomer ³MLCT[d_{z²}(Pt)→ π^* (bpy)] transition in the solution absorption spectrum of Pt(bpy)Cl₂ is complicated by the presence of intense charge-transfer features in this region. Nevertheless, the predicted ν_{monomer} is higher than the energy of the lowest ¹MLCT absorption band ($\nu_{\text{max}} \cong 25400 \text{ cm}^{-1}$) in CH₂Cl₂ solution (Gidney, P. M.; Gillard, R. D.; Heaton, B. T. *J. Chem. Soc., Dalton Trans.* **1973**, 132); this result is consistent with the expected ($z^2 < xz, yz$) ordering of occupied d-orbitals in a PtN₂X₂ complex (Martin, D. S. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1982; Vol. 1, pp. 409-448).
- (46) The **E_⊥c** emission from tetracyanoplatinate salts exhibits a weaker dependence on Pt...Pt separation than the **Elle** emission. Gliemann and Yersin^{2,44} account for this result in terms of the intrinsic differences in the singlet FE (**Elle**) and triplet STE (**E_⊥c**) emitting states. With decreasing Pt...Pt separation, the stabilization of a free exciton by distortion along the Pt chain to form a self-trapped exciton becomes less favorable. At a certain Pt...Pt distance, 3.03 Å for the tetracyanoplatinate salts, the lowest triplet FE state is degenerate with the lowest STE state; thus, the STE states effectively vanish for Pt...Pt distances shorter than <3.0 Å.
- (47) An exciton-coupling description of tetracyanoplatinate spectra also predicts the observed *R*⁻³ dependence, assuming simple dipole-dipole coupling and only

nearest-neighbor interactions.⁴² In this model, the slope is proportional to the transition dipole moment, which is in turn proportional to the electronic transition oscillator strength. Indeed, the oscillator strength of the $d\sigma^* \rightarrow \pi^*$ ¹MLCT transition in face-to-face dimers of Pt(diimine) complexes (Bailey, J. A.; Miskowski, V. M.; Gray, H. B. *Inorg. Chem.* **1993**, 32, 369; see Chapter 5) is weaker than that of the $d\sigma^* \rightarrow p\sigma$ transition of $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4+}$ (Stiegman, A. E.; Rice, S. F.; Gray, H. B.; Miskowski, V. M. *Inorg. Chem.* **1987**, 26, 1112).

- (48) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, 100, 6093.
- (49) The deviations of the data from a linear fit (energy vs. R^{-3} , Figures 4.8-9) far exceed the experimental uncertainties; therefore, we do not report e.s.d.s for equations 3-6.
- (50) Zuleta, J. A.; Chesta, C. A.; Eisenberg, R. *J. Am. Chem. Soc.* **1989**, 111, 8916.
- (51) Crystals of the red form of $\text{Pt}(\text{dmbpy})(\text{ecda})$ (ecda = ethyl-2-cyano-3,3'-dimercaptoacrylate) examined in our laboratory were badly twinned; however, photographs suggest a chain structure with a 3.3 Å metal-metal spacing. Diffuse reflectance spectra show a shoulder near 550 nm that is absent in the yellow form of this compound. The emission maximum (655 nm) was previously reported.⁵⁰
- (52) Extended Hückel calculations of Whango and Hoffman⁴⁸ reproduce the linear R^{-3} dependence of the $d\sigma^* \rightarrow p\sigma$ band gap. Using their values, we find that the energy of the upper edge of the d_{z^2} band exhibits an approximately linear dependence on R^{-3} over the 3.2-3.6 Å range. Thus, an electronic structural model which considers only the dependence of the d_{z^2} band on Pt...Pt separation also predicts the linear R^{-3} dependence of the $d\sigma^* \rightarrow \pi^*$ gap.
- (53) We note that reliable estimates of ν_{monomer} cannot be extracted from so few measurements; for example, a 10% change in m will shift the predicted value of ν_{monomer} by 1-2000 cm^{-1} . Moreover, the validity of extrapolating equations 4.2-4.6 well-beyond the range of measured data is not certain. However, empirically, extrapolations for the tetracyanoplatinate salts² are remarkably reasonable. Thus, it is intriguing to consider that in the limiting case of equal values for m ; then, the energy (ν_{monomer}) of the ³MLCT[$d_{z^2}(\text{Pt}) \rightarrow \pi^*(\text{bpy})$] state of $\text{Pt}(\text{bpy})(\text{CN})_2$ (**4**) is predicted to be ~1600 cm^{-1} *higher* than that of $\text{Pt}(\text{bpy})\text{Cl}_2$ (**2**). This may indicate that the $5d_{z^2}$ level for $\text{Pt}(\text{bpy})(\text{CN})_2$ (**2**) in solution lies at lower energy than for **4**; this prediction does not necessarily disagree with ligand field considerations. The *relative* energies of the $5d_{z^2}$ level in these complexes is not certain; the relative π -donor/acceptor properties of cyanide and chloride which will tend to decrease electron density on the metal in **4** and increase density on the metal in **2**.

- (54) The coefficient of linear thermal expansion is given by $(1/s)(\partial s/\partial T)$, where s is the unit-cell edge length at a given temperature.
- (55) For compounds **6** and **8**, predictions also were made based on the temperature dependence of the polarized emission spectra recorded by Gliemann and co-workers.^{16,24}
- (56) For these estimations, in addition to our assumption that intercomplex electronic coupling is the same for **1-9**, we also have assumed a linear temperature dependence for α , and we have ignored the possibility of phase transitions.
- (57) Martin, D. S. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1982; Vol. 1, 409.
- (58) Coyer, M. J.; Croft, M.; Chen, J.; Herber, R. H. *Inorg. Chem.* **1992**, *31*, 1752.
- (59) Biedermann, J.; Gliemann, G.; Klement, U.; Range, K.-J.; Zabel, M. *Inorg. Chem.* **1990**, *29*, 1884.
- (60) Biedermann, J.; Gliemann, G.; Klement, U.; Range, K.-J.; Zabel, M. *Inorg. Chim. Acta* **1990**, *169*, 63.
- (61) As noted by Miskowski et al.,⁸ this interpretation is entirely consistent with the spectroscopy of the related ruthenium(II) complexes; the lowest MLCT transitions in $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{CN})_6^{4-}$ occur near 460 nm and 200 nm, respectively.
- (62) Cowman, C. D.; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *15*, 2823.
- (63) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 3877.
- (64) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3967.
- (65) Sutton, A. P. *Electronic Structure of Materials*; Claredon Press: Oxford, 1993.
- (66) *Excitons*, Rashba, E. I.; Sturge, M. D. ed.; North Holland Physics Pub.: Amsterdam, 1982.
- (67) Rössler, U.; Yersin, H. *Phys. Rev. B* **1982**, *26*, 3187.
- (68) For example, the low-temperature polarized-emission data of Gliemann's group has been explained in terms of the selection rules (C_{2v} symmetry) and thermal population of the lowest triplet self-trapped exciton states.^{7,16,23,24} These results are equally consistent with the selection rules and thermal population of the lowest $d\sigma^* \rightarrow \pi^*$ triplet states in either a C_{2v} or D_{2h} symmetry scheme.
- (69) Thiel, D. J.; Livins, P.; Stern, E. A.; Lewis, A. *Nature* **1993**, *362*, 40.
- (70) Caspar, J. V.; Westmoreland, T. D.; Allen, G. H.; Bradley, P. G.; Meyer, T. J.; Woodruff, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 3492.
- (71) For example, another explanation for broadened emission profile for $\text{Pt}(\text{dmbpy})(\text{NCO})_2$ (**1**) relates to the larger π^* - $p\sigma$ energy gap and correspondingly smaller extent of π^* - $p\sigma$ mixing expected for chains with longer Pt...Pt spacings;

however, this proposal is not entirely satisfactory since the emission profile remains relatively broad even at 10 K, implying that the breadth is not strictly vibronic.

- (72) Holzapfel, W.; Yersin, H.; Gliemann, G. *J. Chem. Phys.* **1981**, *74*, 2124.
- (73) We arrive at an estimate of the $d\sigma^* \rightarrow p\sigma / d\sigma^* \rightarrow \pi^*$ crossover (2.8 Å) using the linear dependence on R^{-3} of the **El**c emission originating from the $^1d\sigma^* \rightarrow p\sigma$ state ($\nu_{\max}(\text{cm}^{-1}) = 42.9 \times 10^3 - 8.0 \times 10^5 R^{-3}$)² and assuming a 1500 cm^{-1} singlet-triplet splitting; it is arguable that the latter value is an overestimate since the singlet-triplet splitting should decrease for more delocalized excited states. The estimated crossover distance obtained using the dependence of the **EL**c emission is short (2.3 Å), as expected from our discussion in footnote 46.

Chapter 5

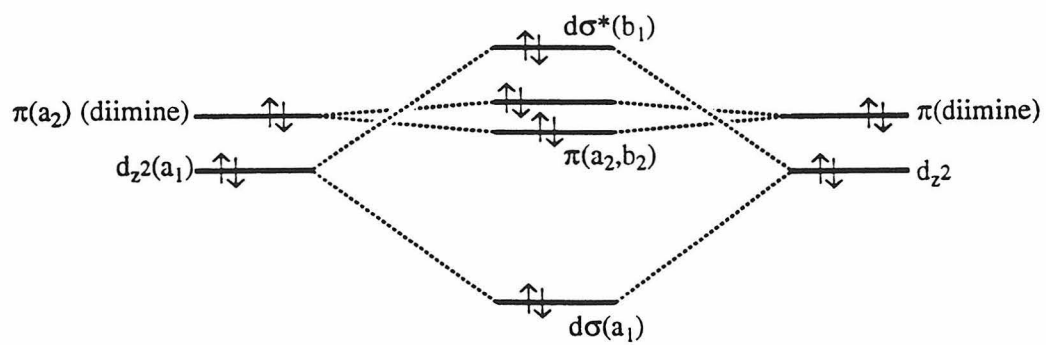
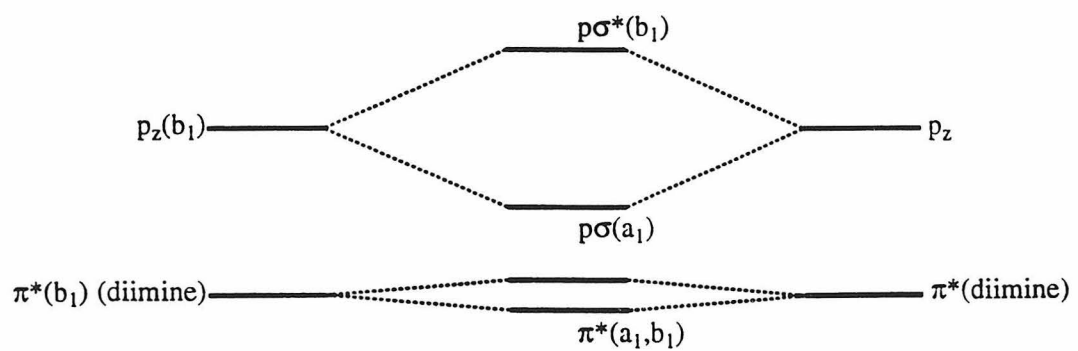
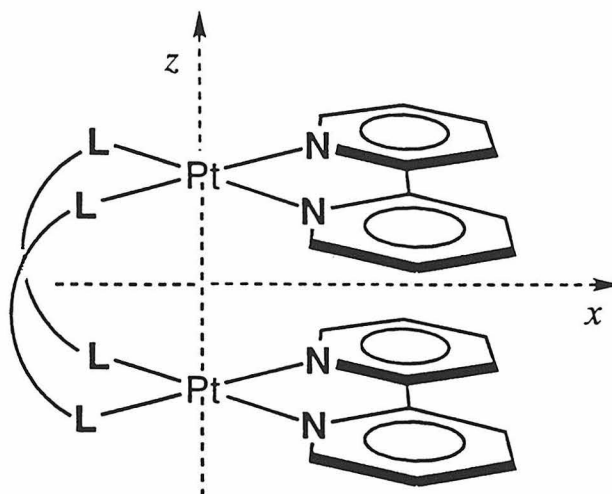
Structure and Spectroscopy of Platinum(II) Bipyridyl Dimers

I. Introduction

Since the earliest studies of $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$, much attention has been given to d^8 - d^8 dimers with emphasis on their potential as photocatalysts.¹⁻³ These complexes are comprised of two bridged square planar metal centers arranged in a face-to-face orientation with relatively short metal-metal contacts ($<3.0 \text{ \AA}$). In this configuration, the orbitals of the adjacent metal centers strongly interact. The fully occupied $5d_{z^2}$ levels split to give bonding ($d\sigma$) and antibonding ($d\sigma^*$) molecular orbitals; similarly, the unoccupied $6p_z$ levels split to give $p\sigma$ and $p\sigma^*$ orbitals (Figure 5.1). Because of the strong $\text{Pt}(d_{z^2})$ interaction, the lowest-energy electronic transition involves excitation of an electron from an antibonding $d\sigma^*$ orbital (d_{z^2} parentage) to a $p\sigma$ orbital (p_z parentage). The resulting $^3d\sigma^* \rightarrow p\sigma$ excited state is frequently long-lived and the excited complex is both a powerful oxidant and reductant. Consequently, these complexes exhibit rich photochemistry that includes electron-transfer and atom-transfer reactions.³

Surprisingly, only a few examples of d^8 - d^8 platinum dimers with polypyridyl ligands are known,⁴⁻¹² and their spectroscopy has not been fully explored. However, our studies of linear-chain platinum(II) diimine complexes leads to an intriguing prediction: the ligand-localized π^* orbital of the diimine is expected to be the LUMO in these complexes (Figure 5.1). We have observed that the emission from the $^3\text{MLCT}[d\sigma^*(\text{Pt}) \rightarrow \pi^*(\text{diimine})]$ state for stacked $\text{Pt}(\text{diimine})\text{X}_2$ complexes is strongly shifted by $3500\text{-}6000 \text{ cm}^{-1}$ to lower energy from the emission from the predominantly metal-centered $^3d\sigma^* \rightarrow p\sigma$ state for stacked $\text{Pt}(\text{CN})_4^{2-}$ complexes. A similar trend is observed for the lowest-energy absorption bands for these compounds; for example, $\text{Pt}(\text{bpy})(\text{NCS})_2$ ($\text{Pt} \cdots \text{Pt}$ $3.30 \text{ \AA}$, $\text{bpy} = 2,2'$ -bipyridine) is red, whereas $\text{Ba}[\text{Pt}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ ($\text{Pt} \cdots \text{Pt}$ $3.32 \text{ \AA}$)¹³ is yellow-green (see Chapter 4). This situation suggests a somewhat unusual electronic structure for a d^8 - d^8 complex involving a lowest $^3\text{MLCT}[d\sigma^* \rightarrow \pi^*]$ excited state. Therefore, the incorporation of diimine ligands into these dimers should provide a means of tuning their photophysics and photochemistry.

Figure 5.1 Qualitative molecular orbital diagram for face-to-face binuclear platinum(II) bipyridyl complexes. C_{2v} symmetry labels are shown in parentheses. For d^8 - d^8 dimers lacking low-lying ligand π^* levels, the $d\sigma^* \rightarrow p\sigma$ transition is the lowest-energy electronic transition. In contrast, the $d\sigma^* \rightarrow \pi^*$ transition is lowest for binuclear Pt(II) bipyridyl complexes.



[illegible]

Recently Lippert and co-workers⁴⁻⁶ have extended this methodology to the preparation of several Pt(II) and mixed-Pt(II)/Pd(II) dimers with bipyridyl ligands, including [(bpy)Pt(μ -MeT)₂Pt(bpy)]²⁺ and [(bpy)Pt(μ -MeT)₂Pt(bpy)]²⁺; unfortunately, only the mixed-ligand [(NH₃)₂Pt(μ -MeU)₂Pt(bpy)](NO₃)₂·3H₂O head-to-head complex (Pt...Pt 2.929(1) Å)⁶ and the palladium(II) [(bpy)Pd(μ -MeT)₂Pd(bpy)](NO₃)₂·5.5H₂O head-to-head complex (Pd...Pd 2.848(1) Å)⁴ have been structurally characterized. Recently, Matsumoto and co-workers^{7,12} have reported the only crystal structures of binuclear

platinum(II) bipyridyl complexes, namely the head-to-tail isomer of $[(bpy)Pt(\mu-\alpha\text{-pyrrolidonate})_2Pt(bpy)](ClO_4)_2$ (Pt...Pt 2.899(2) Å) and the head-to-head isomer of $[(bpy)_2Pt(\mu\text{-dmgi})](NO_3)_2 \cdot 2(H_2O)$ (Pt...Pt 2.833(3), 2.845(3) Å) (dmgi=3,3-dimethylglutarimide). In contrast, there are several structurally characterized examples of bridged platinum(II) terpyridyl dimers.⁸⁻¹¹

It is striking that all of these Pt(II) and Pd(II) dimers with bipyridyl ligands are reported to be red or violet; even the mixed-metal/mixed-ligand derivative $[(NH_3)_2Pt(\mu\text{-MeU})_2Pd(bpy)](NO_3)_2 \cdot 3H_2O$ is reported to form orange-red needles.⁵ For comparison, Pt(II) and Pd(II) bipyridyl monomers are typically yellow or colorless, suggesting the importance of the metal-metal interaction in spectroscopy of the dimers. Furthermore, the corresponding amine $d^8\text{-}d^8$ dimers also are yellow³⁰ (e.g., head-to-tail $[(NH_3)_2Pt(\mu\text{-}\alpha\text{-pyrrolidonate})_2Pt(NH_3)_2](NO_3)_2 \cdot 2H_2O$, Pt...Pt 2.898(1) Å).¹⁸ These observations are entirely consistent with a low-lying $d\sigma^* \rightarrow \pi^*$ transition. In this chapter, we describe the structures and spectroscopy of several novel platinum(II) bipyridyl dimers. Since the spectroscopy and photophysics of monomeric Pt(II) diimine dithiolato complexes are rich, we have investigated complexes with thiolate bridging ligands. Our initial efforts have uncovered surprising isomerism in solution and the solid state.

II. Experimental

Spectroscopic methods are described in Chapter 2. For compounds **2b**, **3a**, **3b**, and **4**, the mass spectra were consistent with the binuclear dication or a mononuclear cation. The bridging ligands, pySH (2-mercaptopyridine) and meimidSH (2-mercapto-1-methyl-imidazole), were purchased from Aldrich; MeTH was obtained from Sigma.

A. Synthesis

1. $[(bpy)Pt(\mu\text{-MeT})_2Pt(bpy)](NO_3)_2$

Following the protocol of Lippert and co-workers,⁴⁻⁶ 0.409 g $Pt(bpy)Cl_2$ and 0.328 g $AgNO_3$ were warmed in 25 ml water, and then filtered to give a yellow filtrate.

Addition of 0.434 g MeT in 2 ml 1 M NaOH, followed by warming for 14 hours at 65° C gave Pt(bpy)(MeT)₂ as a yellow solid with green emission. In a second step, 0.201 g Pt(bpy)Cl₂ and 0.161 g AgNO₃ were warmed in 20 ml water and filtered. After addition of 0.294 g Pt(bpy)(MeT)₂, the mixture was warmed overnight. A small quantity of gray solid was removed by filtration to give deep red solution. Evaporation gave red needles of **1**.

On a separate occasion, 0.389 g Pt(bpy)Cl₂ and 0.280 g AgNO₃ were heated in 80 ml water. The AgCl was removed by filtration and the filtrate was diluted to a volume of ~200 ml. After addition of 0.348 g MeT and 1.75 ml 1M KOH, the solution was stirred with low heat for 30 hours. The pH was adjusted from ~7.5 to 6 with HNO₃ and the solution was stirred overnight. The volume was reduced to 75 ml and a colorless solid was removed by filtration. After several days, yellow and red crystals formed. Crystals of **1** suitable for X-ray diffraction studies were grown from acetonitrile by vapor diffusion of tetrahydrofuran. Analysis (calc): C, 33.02 (33.17); H, 3.03 (3.13); N, 12.06 (12.09).

2. [(bpy)Pt(μ -pyS)₂Pt(bpy)](NO₃)₂

A mixture of 0.035 g Pt(bpy)Cl₂ and 0.028 g AgNO₃ was warmed in 7 ml *N,N*-dimethylformamide (dmf). AgCl was removed by filtration; 0.047 g Pt(bpy)(pyS)₂ (prepared as described in Chapter 2) was added to the filtrate and the mixture was warmed for 2 hours. Removal of solvent gave a deep red solid. Crystals (orange emission) of [(bpy)Pt(μ -pyS)₂Pt(bpy)](NO₃)₂·2.8(H₂O) (**3a**) were grown from an acetonitrile / acetone solution.

Synthetic routes to the head-to-tail or head-to-head forms appeared to give two isomers by ¹H NMR. It was found that an orange product and a violet product could be separated by ion-exchange column chromatography (sepradose FF media, 200-400 mM (NH₄)₂SO₄, pH 7). Precipitation of the orange fraction as the PF₆⁻ salt from an ethanol

extract gave the head-to-tail isomer (**3b**). Heating this compound in solution induces formation of some of the head-to-head isomer (**2a**). Crystals of *both* the red head-to-head (**2a**) and orange head-to-tail (**3b**) PF₆⁻ salts were isolated from the same NMR tube one week *after* the spectrum was collected. Subsequently it was found that fractional crystallization of red acetonitrile solutions containing mixtures of the PF₆⁻ salts allows for separation of orange needles of **3b**. The red-violet aqueous fraction readily converted to an orange solution with heating or extraction with ethanol. Concentration of this solution to dryness using an aspirator *and* applying heat, gave orange and violet solid. When redissolved in ethanol and concentrated *without heat*, the solid was violet (**2b**).

3. [(bpy)Pt(μ -meimidS)₂Pt(bpy)](NO₃)₂

This material was prepared in analogy to the preparation of pyS-bridged dimers in dmf solution. Addition of the meimidSH in NaOH_(aq) ligand immediately gave a deep red solution. The dark red nitrate salt (**4**) precipitated during concentration. (Addition of K(PF₆)_(aq) precipitated an orange solid that was not examined.) The ¹H NMR spectrum is consistent with a single species at high concentration. However, the UV-visible absorption spectrum indicates a monomer-dimer (dimer λ_{max} , 545 nm) equilibrium as observed for **2**.

B. X-ray Crystallography

Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer (MoK α radiation and graphite monochromator). Intensities were corrected for Lorentz and polarization effects, as well as for absorption (Ψ scans of six reflections). The intensities of three standard reflections showed no variations greater than those predicted by counting statistics. The Pt coordinates were obtained from Patterson maps, and remaining non-hydrogen atom positions were determined from successive structure-factor, Fourier calculations. The structures of **1** and **3a** were refined using the CRYM crystallographic computing system;³¹ the structures of **2a** and **3b** were refined using

Table 5.1. Summary of crystal data and structure determination information for **1** and **2a**.

Compound	1 (μ -MeT, head-to-head)	2a (μ -pyS, head-to-head)
Formula	Pt ₂ C ₃₂ H ₃₄ N ₁₀ O ₁₃	Pt ₂ C ₃₀ H ₂₄ N ₆ S ₂ P ₂ F ₁₂
Formula Weight, amu	1156.8	1212.8
Color	red	red
Crystal size (mm)	0.23 x 0.19 x 0.44	0.15 x 0.07 x 0.05
Crystal System	Triclinic	Orthorhombic
Space Group (No.)	<i>P1bar</i> (2)	<i>Pbcn</i>
<i>a</i> , Å	12.160(2)	27.182(7)
<i>b</i> , Å	12.812(4)	14.007(4)
<i>c</i> , Å	14.519(10)	20.578(4)
α , °	67.26(3)	—
β , °	68.28(2)	—
γ , °	67.52(2)	—
<i>Z</i>	2	8
<i>V</i> , Å ³	1860.9(10)	7834(3)
<i>D</i> _{calc} , g cm ⁻³	2.065	2.064
μ , cm ⁻¹	76.63	74.37
Secondary Extinction	0.05(2) x 10 ⁻⁶	—
θ -range, °	1 - 20	1 - 22
Octants Collected	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
No. Reflections	3465	4773
No. Refined Parameters	510	487
<i>R</i> ^a	0.037	0.118
<i>R</i> _w ^b	0.077	0.1072
GOF ^c	2.91	1.764

^a $R = \sum ||F_{\text{obs}}| - |F_{\text{c}}|| / \sum |F_{\text{obs}}|$.³²

^b $R_w = \left(\sum w(F_{\text{obs}}^2 - F_{\text{c}}^2)^2 / \sum w(F_{\text{obs}}^2) \right)^{1/2}$.

^c $\text{GOF} = \left(\sum w(F_{\text{obs}}^2 - F_{\text{c}}^2)^2 / (n - p) \right)^{1/2}$ where *n* and *p* are the number of observations and parameters, respectively.

Table 5.2. Summary of crystal data and structure determination information for **3a** and **3b**.

Compound	3a (μ -pyS, head-to-tail)	3b (μ -pyS, head-to-tail)
Formula	Pt ₂ C ₃₀ H _{29.6} N ₈ S ₂ O _{8.8}	Pt ₂ C ₃₀ H ₂₄ N ₆ S ₂ P ₂ F ₁₂
Formula Weight, amu	1097.8	1212.8
Color	red	orange
Crystal size (mm)	—	0.40 x 0.15 x 0.04
Crystal System	Monoclinic	Monoclinic
Space Group (No.)	<i>P2₁/c</i>	<i>P2₁/n</i>
<i>a</i> , Å	11.179(3)	21.429(8)
<i>b</i> , Å	13.511(4)	7.3940(1)
<i>c</i> , Å	24.138(5)	24.824(9)
α , °	—	—
β , °	99.52(2)	113.90(3)
γ , °	—	—
<i>Z</i>	4	4
<i>V</i> , Å ³	3596(2)	3596(2)
<i>D</i> _{calc} , g cm ⁻³	2.028	2.240
μ , cm ⁻¹	80.25	80.73
Secondary Extinction	—	1.6 x 10 ⁻⁴ (3)
θ -range, °	1 - 25	1 - 22.5
Octants Collected	$\pm h, \pm k, \pm l$	$+h, \pm k, \pm l$
No. Reflections	3858	4659
No. Refined Parameters	384	488
<i>R</i> ^a	0.0721	0.100
<i>R</i> _w ^b	0.096	0.099
GOF ^c	2.17	1.70

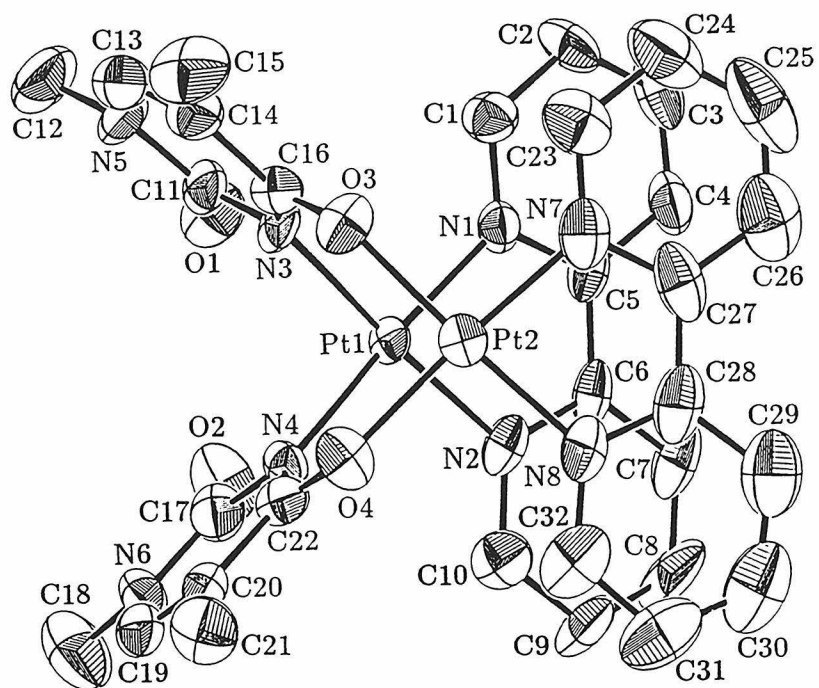
^a $R = \sum ||F_{\text{obs}}| - |F_{\text{c}}|| / \sum |F_{\text{obs}}|$.³²

^b $R_w = \left(\sum w(F_{\text{obs}}^2 - F_{\text{c}}^2)^2 / \sum w(F_{\text{obs}}^2) \right)^{1/2}$.

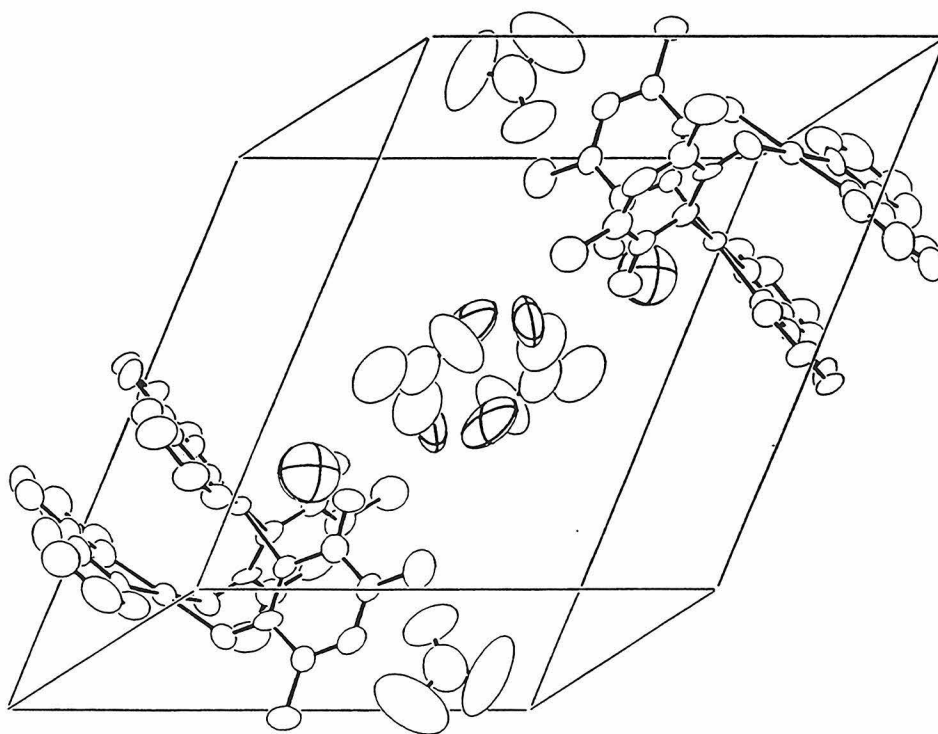
^c GOF = $\left(\sum w(F_{\text{obs}}^2 - F_{\text{c}}^2)^2 / (n - p) \right)^{1/2}$ where *n* and *p* are the number of observations and parameters, respectively.

Figure 5.2 Drawings of the head-to-head dications with 50% probability ellipsoids and the crystal packings for: (a,b) $[(\text{bpy})\text{Pt}(\mu\text{-MeT})_2\text{Pt}(\text{bpy})](\text{NO}_3)_2 \cdot 3(\text{H}_2\text{O})$ (**1**) and (c,d) $[(\text{bpy})\text{Pt}(\mu\text{-pyS})_2\text{Pt}(\text{bpy})](\text{PF}_6)_2$ (**2a**).

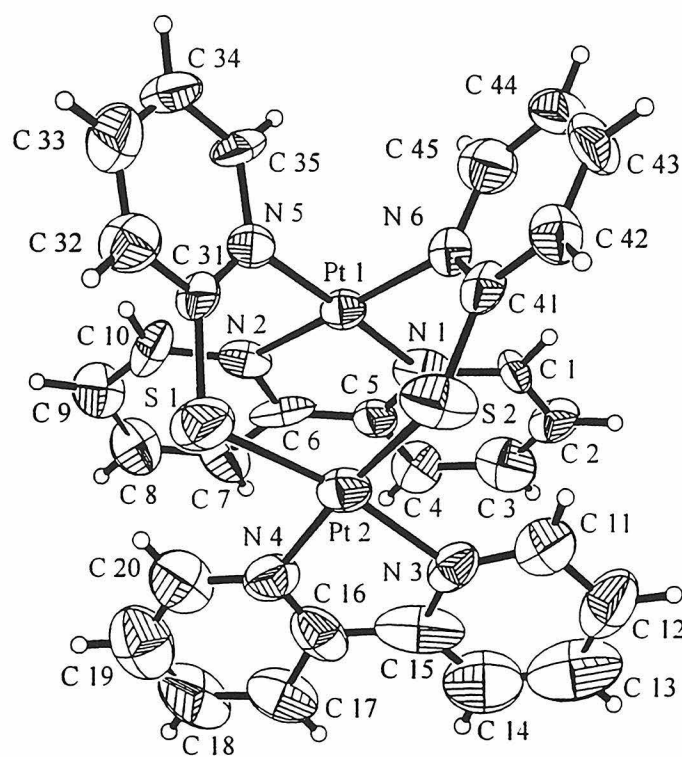
(a)



(b)



(c)



(d)

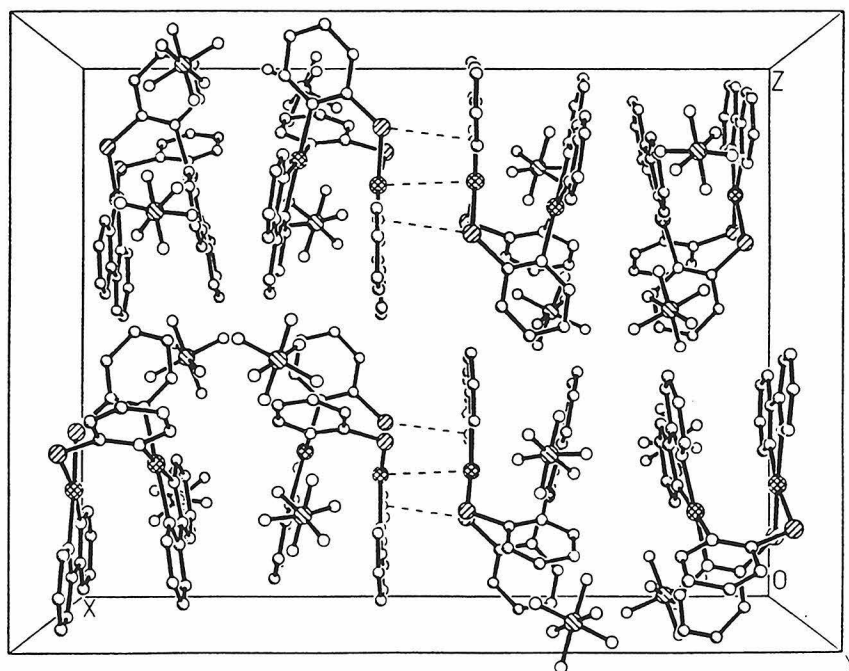
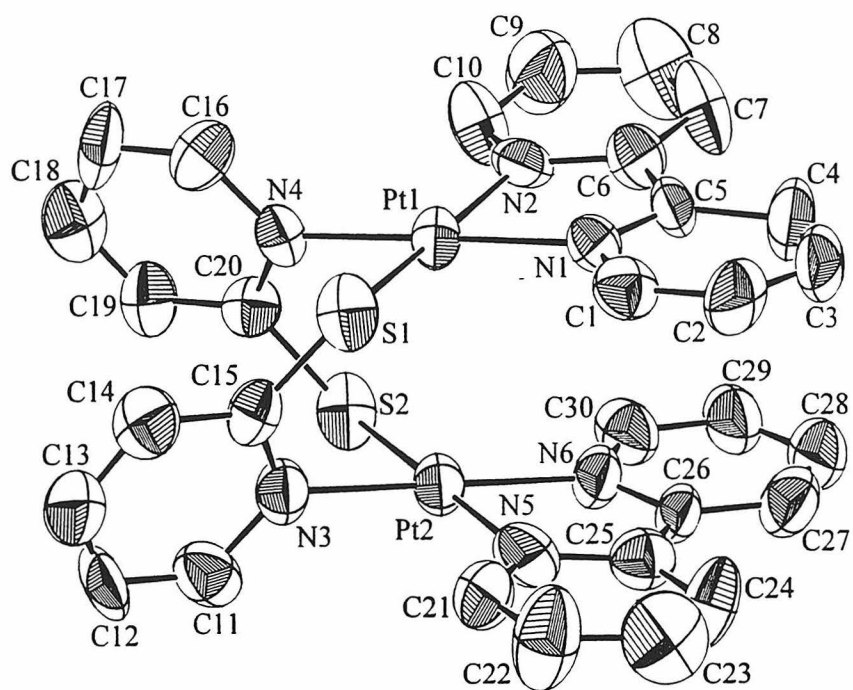
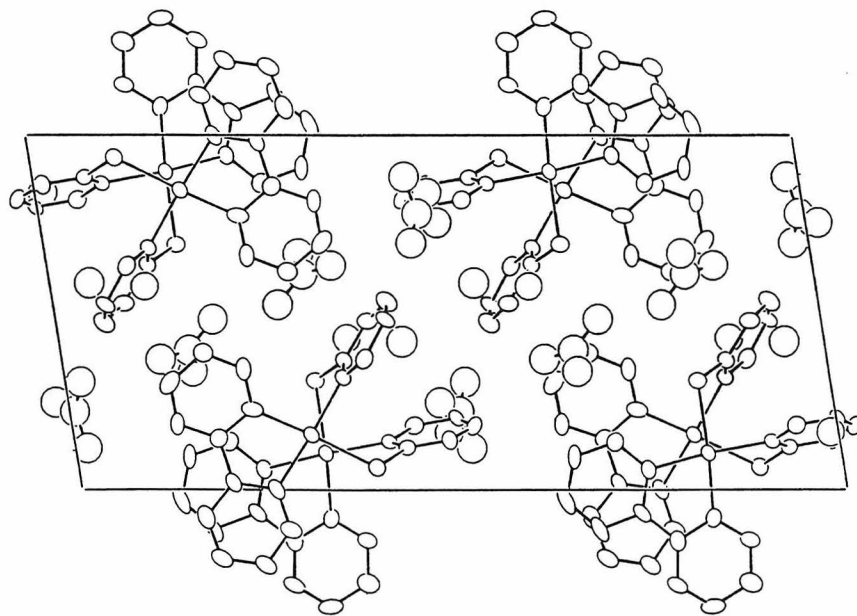


Figure 5.3 Drawings of the head-to-tail dications with 50% probability ellipsoids and the crystal packings for: (a,b) $[(\text{bpy})\text{Pt}(\mu\text{-pyS})_2\text{Pt}(\text{bpy})](\text{NO}_3)_2 \cdot 2.8(\text{H}_2\text{O})$ (**3a**) and (c,d) $[(\text{bpy})\text{Pt}(\mu\text{-pyS})_2\text{Pt}(\text{bpy})](\text{PF}_6)_2$ (**3b**).

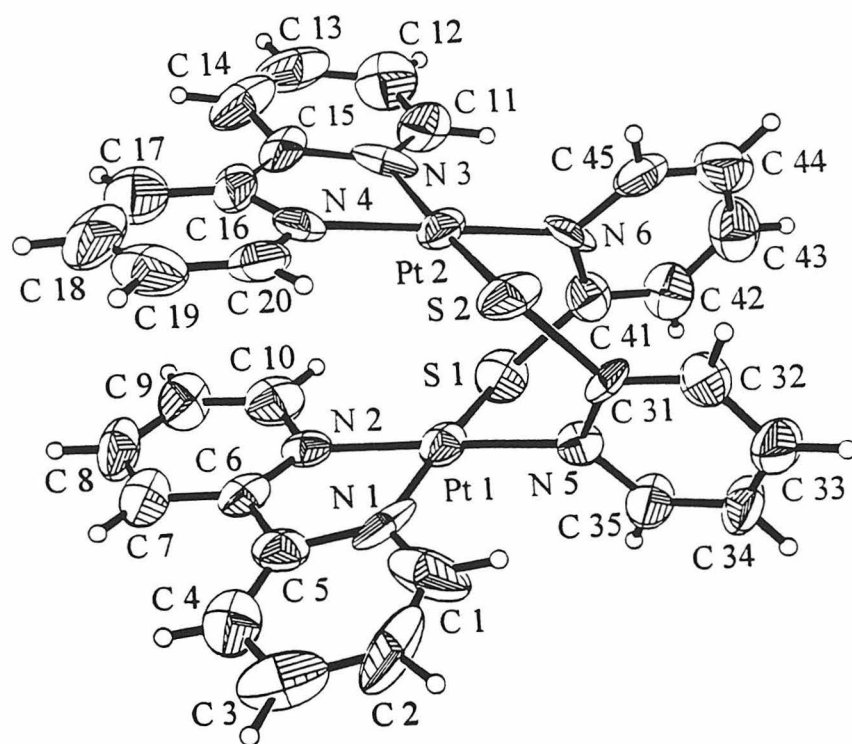
(a)



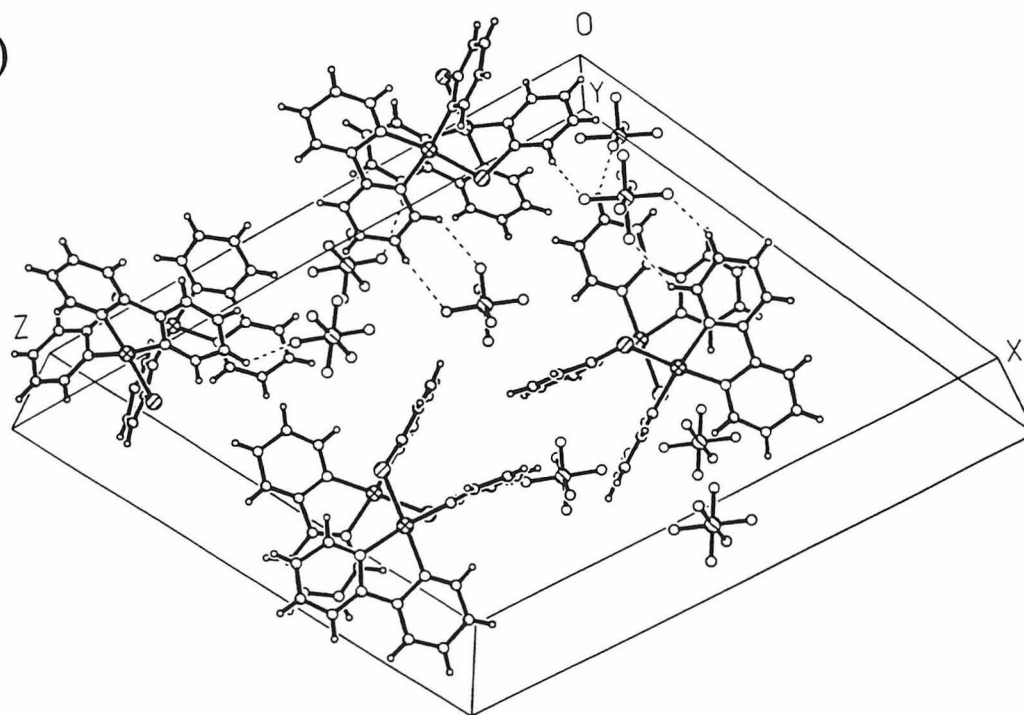
(b)



(c)



(d)



SHELXS-93.³³ For **1** and **3a** ligand H atoms were positioned by calculation (C-H, 0.95 Å) and were assigned isotropic B's 1.15 times those of the attached carbon atoms; for **2a** and **3b**, H atoms were included in the least squares as riding atoms. Pertinent experimental data are collected in Tables 1-2 and bond distances and angles are given in Tables 5.3-4. Full details of these structures are available from the Caltech X-ray Crystallography Facility.

III. Results and Discussion

A. Structures

The structures of four platinum(II) bipyridyl dimers have been determined: the head-to-head isomers of [(bpy)Pt(μ -MeT)₂Pt(bpy)](NO₃)₂·3(H₂O) (**1**) and [(bpy)Pt(μ -pyS)₂Pt(bpy)](PF₆)₂ (**2a**); and the head-to-tail isomers of [(bpy)Pt(μ -pyS)₂Pt(bpy)](NO₃)₂·2.8(H₂O) (**3a**) and [(bpy)Pt(μ -pyS)₂Pt(bpy)](PF₆)₂ (**3b**). Crystals of **1**, **2a**, and **3a** are red, whereas crystals of **3b** are orange; we emphasize that the cations for **3a** and **3b** are chemically equivalent, but the anions and water content are different.

Selected distances and angles are shown in Tables 5.3 and 5.5. The ligand geometries are normal. For structures of **2-3**, several factors contribute to the uncertainty in the positions of the light atoms; the resulting distances and angles are imprecise as suggested by the e.s.d.s. The crystal of **2a** was very small (0.15 x 0.07 x 0.05 mm), resulting in weak diffraction data. In the case of **3b**, the fibrous nature of the crystal probably affected the quality of the diffraction data. For **3a**, the water molecules and nitrates are disordered.

1. [(bpy)Pt(μ -MeT)₂Pt(bpy)](NO₃)₂·3(H₂O) (**1**)

The Pt atoms are bridged by two MeT groups arranged in a head-to-head configuration with a Pt···Pt separation of 2.849(1) Å (Figure 5.2a). The average of the four torsion angles along the Pt···Pt vector (ω) is 2.0(8)° (scatter e.s.d.); thus, the two square planar units are stacked in a nearly eclipsed arrangement. The two coordination

Table 5.3. Selected distances (Å) and angles (°) for **1** and **2a**.

[Pt(bpy)(μ -MeT)] ₂ (NO ₃) ₂ ·3(H ₂ O) (1)			
Pt1...Pt2	2.849(1)	N1-Pt1-N2	80.3(4)
Pt1-N1	2.019(10)	N1-Pt1-N3	95.8(4)
Pt1-N2	2.010(10)	N1-Pt1-N4	176.5 [°] (4)
Pt1-N3	2.052(10)	N2-Pt1-N3	176.1(4)
Pt1-N4	2.054(9)	N2-Pt1-N4	96.2(4)
Pt2-N7	1.959(12)	N3-Pt1-N4	87.7(4)
Pt2-N8	1.968(11)	N7-Pt2-N8	81.5(5)
Pt2-O3	2.019(8)	N7-Pt2-O3	95.7(4)
Pt2-O4	2.013(9)	N7-Pt2-O4	176.5 [°] (4)
N3-C16	1.362(15)	N8-Pt2-O3	177.1(4)
O3-C16	1.254(15)	N8-Pt2-O4	95.4(4)
N4-C22	1.372(15)	O3-Pt2-O4	87.4(3)
O4-C22	1.257(15)	Pt1-N3-C16	123.7(8)
C11-O1	1.222(16)	Pt1-N4-C22	123.2(8)
C17-O2	1.213(17)	Pt2-O3-C16	129.5(8)
		Pt2-O4-C22	130.4(8)
O4-C22-N4	121.9(11)	O3-C16-N3	122.5(11)
[Pt(bpy)(μ -pySl) ₂ (PF ₆) ₂ (2a)			
Pt1...Pt2	2.924(1)	N1-Pt1-N2	82.1(8)
Pt1-N1	2.07(2)	N1-Pt1-N6	97.1(7)
Pt1-N2	2.03(1)	N1-Pt1-N5	176.8(7)
Pt1-N5	2.04(2)	N2-Pt1-N6	177.8(6)
Pt1-N6	2.04(2)	N2-Pt1-N5	94.7(6)
Pt2-N3	2.09(2)	N5-Pt1-N6	86.1(5)
Pt2-N4	2.02(2)	N3-Pt2-N4	78.8(9)
Pt2-S1	2.291(6)	N3-Pt2-S2	98.0(7)
Pt2-S2	2.261(6)	N3-Pt2-S1	170.4(6)
N5-C31	1.34(2)	N4-Pt2-S2	172.9(5)
C31-CS1	1.72(2)	N4-Pt2-S1	92.5(7)

N6-C41	1.34(2)	S1-Pt2-S2	90.1(2)
C41-S2	1.75(2)	Pt1-N5-C31	123.1(12)
		Pt1-N6-C41	124.2(13)
S1-C31-N5	117(2)	Pt2-S1-C31	113.4(7)
S2-C41-N6	117(2)	Pt2-S2-C41	115.7(7)

planes, defined by a Pt and its four coordinated atoms, form a dihedral angle (τ) of $22.1(3)^\circ$. Each Pt atom deviates by less than $0.02 \text{ \AA}$ from the plane defined by its four coordinated atoms. The Pt...Pt separation is longer than the intraligand distances ($2.29(1)$, $2.30(1) \text{ \AA}$) between the coordinated N and O atoms of the MeT groups. Thus, the splay of the coordination planes is consistent with a slight deviation of the bridging bond angles from 120° (e.g., Pt2-O-C, $129.5(9)$, $130.4(8)^\circ$). The approximately planar bipyridyl ligand bound to Pt1 lies in the corresponding coordination plane. In contrast, the bipyridyl ligand bound to Pt2 is slightly tilted out of the coordination plane *toward* the bipyridyl ligand bound to Pt1; consequently, the planes defined by the bipyridyl ligands form a dihedral angle ($11.1(4)^\circ$) that is slightly smaller than τ . We see no obvious reason for this tilt, but it may be related to crystal packing effects (Figure 5.2b). We note, however, that the Pt2-N(bpy) distances are shorter than the Pt1-N(bpy) distances by $\sim 0.05\text{--}6 \text{ \AA}$, as expected from trans influence considerations.

Table 5.4 lists some structural properties of pyridonate and pyrimidinate bridged platinum(II) dimers. While the Pt...Pt separation in **1** is typical for Pt(II) dimers, it is striking that it is shorter than found for any of the previously reported Pt(II) amine head-to-head dimers with *cis* MeT, MeU or α -pyridonate (pyr) bridging ligands. Nevertheless, this distance and the τ and ω angles are very similar to the values reported for $[(\text{NH}_3)_2\text{Pt}(\mu\text{-MeT})_2\text{PtCl}_2](\text{NO}_3)_2 \cdot 3(\text{H}_2\text{O})$.⁴ The Pt...Pt separation ($2.899(2) \text{ \AA}$) for $[\text{Pt}(\text{bpy})_2(\mu\text{-pyrrolidonate})_2](\text{ClO}_4)_2$ also is somewhat shorter than found for related dimers (e.g., $[\text{Pt}(\text{NH}_3)_4(\mu\text{-pyrrolidonate})_2]_2(\text{PF}_6)_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$).^{7,34} In fact, diimine π -backbonding is expected to stabilize the Pt...Pt interaction by decreasing electron density

on the metals, thereby reducing electronic repulsions between the platinum centers. However, the Pt...Pt distance is nearly identical to the Pd...Pd distance found for the Pd(II) analogues,⁴ [(bpy)Pd(μ -MeT)₂Pd(bpy)](NO₃)₂·5.5(H₂O) and [Pd(bpy)(μ -dmgi)]₂(NO₃)₂·2(H₂O).¹² Thus, the shorter metal-metal separation is entirely consistent with weaker steric repulsions associated with the bipyridyl ligands.

Table 5.4. Geometrical properties of some head-to-head *cis*-pyrimidinate, pyridinate, pyrrolidonate, and glutarimide bridged Pt(II) dimers, and the head-to-tail [Pt(bpy)(μ -pyrrolidonate)]₂(ClO₄)₂ dimer.^c

Compound (color)	Pt...Pt, Å	τ , ° ^a	ω , ° ^b	reference
[Pt(en)(μ -pyr)] ₂ (NO ₃) ₂ (yellow)	2.992(1)	39.6	24.9	20
[(NH ₃) ₂ Pt(μ -MeT) ₂ Pt(NH ₃)Cl]	2.939(1)	31.5	0.8	4
[Pt(NH ₃)Cl ₃]·H ₂ O (yellow-green)				
[Pt(NH ₃) ₂ (μ -MeU)] ₂ (NO ₃) ₂ (yellow)	2.937(1)	34.1	25.2	15
[(NH ₃) ₂ Pt(μ -MeU) ₂ Pt(bpy)](NO ₃) ₂ (red)	2.929(1)	30.4	10.2	6
[Pt(NH ₃) ₂ (μ -MeT)] ₂ (NO ₃) ₂ (yellow)	2.927(1)	31.4	1.9	16,19
[Pt(bpy)(μ -pyrrolidonate)] ₂ (ClO ₄) ₂	2.899(2)	21.1	7.5	7
[Pt(NH ₃) ₂ (μ -pyr)] ₂ (NO ₃) ₂ (yellow)	2.877(1)	30.0	20.3	18
[(NH ₃) ₂ Pt(μ -MeT) ₂ PtCl ₂](NO ₃) ₂ ·3(H ₂ O) (light red) ³⁰	2.861(1)	22.5	3.0	4
[(bpy)Pt(μ -dmgi) ₂ Pd(bpy)](NO ₃) ₂ ·H ₂ O (red)	2.854(2)	NA	NA	12
[Pt(bpy)(μ -MeT)] ₂ (NO ₃) ₂ ·3(H ₂ O) (1) (red)	2.849(1)	22.1(3)	2.0(8)	d
[Pd(bpy)(μ -dmgi)] ₂ (NO ₃) ₂ ·2(H ₂ O) (orange)	2.844(2)	NA	NA	12
[(bpy) ₂ Pt(μ -dmgi)](NO ₃) ₂ ·2(H ₂ O) (violet)	2.833(3)	NA	NA	12
	2.845(3) ^e			

^a τ is the tilt angle between Pt coordination planes.

^b ω is the average torsion angle about the Pt...Pt vector.

^c pyrH= α -pyridone; MeTH=1-methylthymine; MeUH=1-methyluracil; dmgi=3,3-dimethylglutarimide.

^d This work.

^e Two dimers in the asymmetric unit.

2. $[(bpy)Pt(\mu\text{-pyS})_2Pt(bpy)](PF_6)_2$ (**2a**)

Two mercaptopyridinate (pyS) ligands bridge the Pt centers in a head-to-head arrangement with a resulting Pt...Pt separation of 2.924(1) Å (Figure 5.2c). The average of the four torsion angles along the Pt...Pt vector (ω) is 14(2)° (scatter e.s.d.), indicating a slight twisting about the Pt...Pt vector. Pt1 and Pt2 are slightly displaced toward each other (0.014(7) and 0.104(6) Å, respectively) from the planes defined by their four coordinated atoms; such displacements are not uncommon in structures of d⁸-d⁸ dimers, and they are consistent with a weak bonding interaction between metal centers. The N-S intraligand distances (2.72(2), 2.73(2) Å) are longer than the intraligand N...O distances of pyrimidinate and pyridonate ligands (~2.3 Å); consequently, the two coordination planes, defined by a Pt and its four coordinated atoms, form a smaller dihedral angle (τ , 13.8(2)°) than found for dimers with those bridging ligands (Table 5.3). Interestingly, for idealized bond angles (C, N, sp²; S, sp³ hybridization), the bipyridyl ligands are predicted to tilt *toward* each other (τ , -15°).³⁵ The molecule avoids the unfavorable close approach of the Pt(bpy) units by twisting; a scale model of the dication reveals that twisting about the Pt...Pt vector - that is, increasing ω - reduces overlap between the bipyridyl ligands and splay the coordination planes, causing τ to increase. Indeed, values of τ , ω and the Pt...Pt distance are among the smallest found for the *cis*-mercaptopyridinate and related bridged Pt and Pd dimers (Table 5.5).

The dications pack in pairs to form tetramers with relatively short intermolecular Pt2...Pt2 contacts (3.419(1) Å). The dimers are related by a twofold axis resulting in a staggered stacking arrangement as observed for the platinum(II) diimine linear-chain structures. Binuclear platinum(II) complexes are known to form tetramers of this type.^{12,18,20} There are short contacts between the S atoms and the bipyridyl ligands (S1-N4, 3.27(2); S1-C16, 3.36(2); 3.38(2); S2-C11, 3.37(2) Å). Interestingly, the bipyridyl ligand bound to Pt2 is tilted slightly out of the coordination plane toward the S atoms of the adjacent complex, suggesting charge-transfer interactions (Figure 5.2d).

3. $[(bpy)Pt(\mu\text{-pyS})_2Pt(bpy)](NO_3)_2 \cdot 2.8(H_2O)$ (**3a**)

Though the two mercaptopyridinate ligands bridge the Pt centers in a head-to-tail arrangement (Figure 5.3a), the resulting 2.925(1) Å Pt...Pt separation is nearly identical with that of the head-to-tail isomer (**2a**, 2.924(1) Å). However, **3a** is considerably more twisted about the Pt...Pt vector (ω , 35.0(4)° (scatter e.s.d.); see Table 5.5); consequently, the two coordination planes form a slightly larger dihedral angle (τ , 16.5(4)°) than found for **2a** (13.8(2)°). Pt1 and Pt2 are only slightly displaced toward each other (<0.02 Å) from the planes defined by their four coordinated atoms. Though this twisting can reduce steric repulsions between the bipyridyl ligands, the 6(2)° dihedral angle formed by the two planes defined by the bipyridyl ligands is *smaller* than τ . In fact, the shortest intradimer bpy-bpy contacts are relatively long (C1-C25, 3.39(3); C6-C30, 3.44(3); C1-N5, 3.48 Å) and would be considered reasonable for *intermolecular* contacts.

The nitrates and water groups are disordered in this structure. This situation can lead to ambiguity in the assignment of Pt oxidation states, since the ratio of anions to dications is not firmly established by the crystallography. We have considered the possibility of an oxidized dimer, but we find that the structural features (as well as the chemical properties) of **3a** are inconsistent with this hypothesis. Partially oxidized Pt dimers tend to form metal oligomers (tetramers,^{21,26} octamers,^{27,28} etc.); however, the complexes in **3a** do not stack and there are no short *interdimer* Pt...Pt interactions. In addition, the intradimer Pt...Pt distance is expected to contract with partial oxidation since the metal-metal interaction becomes formally bonding; however, the metal-metal separation in **3a** is typical of Pt(II) dimers (Tables 5.3-4) and nearly identical to that of **2a** for which the counterions are not disordered. Moreover, we find no evidence of Pt-axial ligand interactions that characterize structures of oxidized Pt dimers.

Table 5.5. Selected distances (Å) and angles (°) for head-to-tail dimers in **3a** and **3b**.

[Pt(bpy)(μ -pyS)] ₂ (NO ₃) ₂ ·2.8(H ₂ O) (3a)		[Pt(bpy)(μ -pyS)] ₂ (PF ₆) ₂ (3b)	
Pt1...Pt2	2.925(1)	Pt1...Pt2	3.022(1)
Pt1-N1	2.021(14)	Pt1-N1	1.90(2)
Pt1-N2	2.024(10)	Pt1-N2	2.024(10)
Pt1-N4	2.057(13)	Pt1-N5	2.057(13)
Pt1-S1	2.288(5)	Pt1-S1	2.288(5)
Pt2-N5	2.005(17)	Pt2-N3	2.070(14)
Pt2-N6	2.034(15)	Pt2-N4	2.005(17)
Pt2-N3	2.070(14)	Pt2-N6	2.034(15)
Pt2-S2	2.297(5)	Pt2-S2	2.297(5)
S1-C15	1.706(18)	S1-C41	1.706(18)
S2-C20	1.748(18)	S2-C31	1.748(18)
N3-C15	1.34(2)	N6-C41	1.34(2)
N4-C20	1.31(2)	N5-C31	1.31(2)
N1-Pt1-N2	80.1(6)	N1-Pt1-N2	78.3(6)
N1-Pt1-S1	95.9(4)	N2-Pt1-S1	97.5(5)
N1-Pt1-N4	175.1(5)	N2-Pt1-N5	174.4(6)
N2-Pt1-S1	174.4(4)	N1-Pt1-S1	170.2(4)
N2-Pt1-N4	96.0(5)	N1-Pt1-N5	96.3(6)
N4-Pt1-S1	88.2(4)	N5-Pt1-S1	88.1(4)
N5-Pt2-N6	80.7(7)	N3-Pt2-N4	80.0(7)
N6-Pt2-S2	95.7(7)	N4-Pt2-S2	97.4(5)
N6-Pt2-N3	176.4(6)	N4-Pt2-N6	171.6(6)
N5-Pt2-S2	175.4(5)	N3-Pt2-S2	172.9(4)
N3-Pt2-N5	96.0(6)	N3-Pt2-N6	92.8(6)
N3-Pt2-S2	87.6(4)	N6-Pt2-S2	90.2(4)
Pt1-N4-C20	124.0(11)	Pt1-N5-C31	120.8(9)
Pt2-N3-C15	120.0(12)	Pt2-N6-C41	121.3(11)
Pt1-S1-C15	105.9(6)	Pt1-S1-C41	106.8(6)
Pt2-S2-C20	107.5(6)	Pt2-S2-C31	104.6(6)
S1-C15-N3	123.3(13)	S1-C41-N6	118.7(14)
S2-C20-N4	120.3(13)	S2-C31-N5	118.5(11)

4. $[(bpy)Pt(\mu-pyS)_2Pt(bpy)](PF_6)_2$ (**3b**)

While crystals of **3a** are red, crystals of **3b** are bright orange. The only differences in chemical composition are the counterions and solvent of crystallization; yet, there are no unusually short intermolecular interactions in either structure. Indeed, the origin of these differences in color lies in the geometry of the dimers. The Pt...Pt separation is ~0.1 Å longer in crystals of **3b** (3.022(1) Å) than in crystals of **3a** (2.925(1) Å). The longer metal-metal distance is accompanied by a larger dihedral angle (τ , 21.3(3)°) formed by the coordination planes. Also, the Pt atoms are somewhat more displaced toward each other from the planes defined by their four coordinated atoms (0.070(5), 0.027(5) Å). Notwithstanding, the bond distances and angles for both compounds are very similar (Table 5.6). It appears that the larger twisting about the Pt...Pt vector in crystals of **3b** leads to a longer metal-metal separation; ω is 45(2)° for **3b** and 35.0(4)° for **3a**. In fact, a scale model of the dication reveals that twisting about the Pt...Pt vector splay the coordination planes causing τ and the Pt...Pt separation to increase. The differences in ω and τ in **3a** and **3b** suggests that the potential energy surface along this twisting coordinate is shallow. Thus, we have an example of conformational polymorphism;³⁶⁻³⁸ however, in contrast to cases involving organic molecules with many degrees of freedom, a dramatic color change accompanies the conformational change in these Pt dimers. A somewhat similar situation has been observed for salts of the d⁸-d⁸ dication, Rh₂(dimen)₄²⁺ (dimen=1,8-diisocyanomethane). Because of the flexibility of the bridging ligands, the Rh...Rh distance varies from 4.48 Å (PF₆⁻) to 3.86 Å (tetraphenylborate) depending on the anion; the twist angle about the Rh...Rh vector increases with metal-metal contraction (0-16.2°).^{39,40}

It is clear that the dimers in **3b** are considerably more twisted than related *cis*-mercaptopyridinate-bridged Pt(II) and Pd(II) complexes (Table 5.6). In addition, it appears that the conformations of the dications are related to the crystal packings. One

possibility is that the distorted conformation of the dications in **3b** is adopted in order to allow for more efficient packing with the PF_6^- anions. Indeed, the displacement of the Pt atoms toward each other from their coordination planes is consistent with a less favorable $\text{Pt}\cdots\text{Pt}$ separation. In contrast, the water and small nitrate anions in **3a** may provide greater packing flexibility, allowing the dications and anions to efficiently pack with less elongation of the metal-metal interaction.

It also is remarkable that **3b** is 8.5% denser than crystals of **2a** which contain pairs of weakly interacting head-to-head dications and PF_6^- anions. The only compositional difference between these materials is that **3b** contains the head-to-tail dimer and **2a** contains the head-to-head dimer. This result is consistent the expectation that directed intermolecular interactions can offset packing inefficiencies.

Table 5.6. Geometrical properties of *cis*-mercaptopyridinate and related ligand bridged Pt(II) and Pd(II) dimers.^c

Compound	M $\cdots$ M, Å	τ , ° ^a	ω , ° ^b	reference
[Pt(en) ₂ (μ -4-methyl-pyS)] ₂ (PF ₆) ₂ , HH	3.101(1)	31.0(3)	34.2	41,42
[Pt(en)(μ -pyS)] ₂ Cl ₂ ·3H ₂ O, HH	3.083(1)	31.9(2)	32.6	41,42
[Pt(bpy)(μ -pyS)] ₂ (PF ₆) ₂ (2a), HH	2.924(1)	13.8(2)	2.0(8)	d
[Pt(bpy)(μ -pyS)] ₂ (PF ₆) ₂ (3b), HT	3.022(1)	21.3(3)	45(2)	d
[Pd(dba)(μ -2-quinoline-2-thiolate)] ₂ , HT	2.992	24.6	27(2)	43
[PdCl(PMePh ₂)(μ -pyS)] ₂ , HT	2.982(3)	28.9	18.8	44
[PtCl(μ -aps)] ₂ Cl ₂ ·3H ₂ O, HT ^e	2.956(1)	17.9(4)	3.4(2) ^e	41,42
[PdCl(PMe ₃)(μ -pyS)] ₂ , HT	2.942(2)	24.9	15.6(9)	45
[Pt(bpy)(μ -pyS)] ₂ (NO ₃) ₂ ·2.8(H ₂ O) (3a), HT	2.925(1)	16.5(4)	35.0(4)	d
[PdCl(PMe ₂ Ph)(μ -pyS)] ₂ , HT	2.921(2)	24.5	17(1)	44

^a τ is the tilt angle between Pt coordination planes.

^b ω is the average torsion angle about the Pt $\cdots$ Pt vector; scatter e.s.d. is given in parentheses.

^c dba=*N,N*-dimethylbenzylamine; aps=2-aminoethyl-2-pyridyl sulfide.

^d This work.

^e The aps ligand is tridentate, chelating one metal with the aminoethyl-sulfide group and binding the other with pyridyl group. Strain in the Pt-aminoethyl-sulfide ring restricts twisting about the Pt $\cdots$ Pt vector (*i.e.*, ω must remain near zero).⁴²

B. Electronic Structure

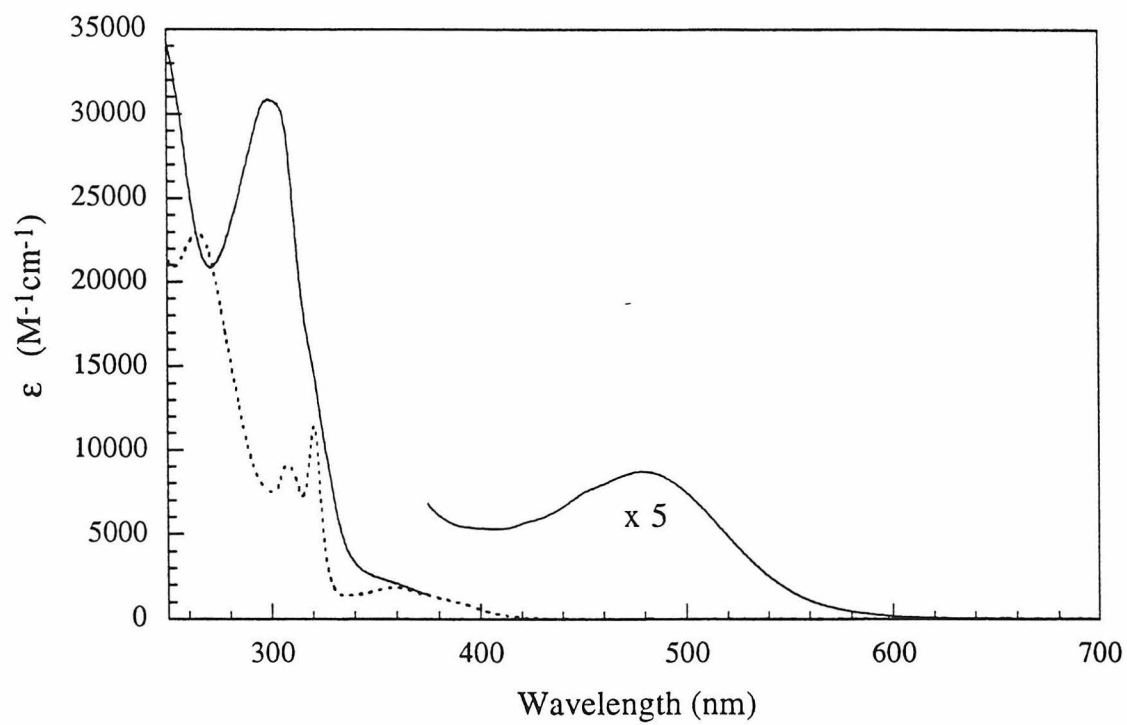
1. $Pt(bpy)(\mu\text{-MeT})_2Pt(bpy)](NO_3)_2 \cdot 3(H_2O)$ (**1**)

The NO_3^- and PF_6^- salts of the $[(bpy)Pt(\mu\text{-MeT})_2Pt(bpy)]^{2+}$ ion form red solids that dissolve in polar solvents to give red-orange solutions (Figure 5.4a). The crystal structure of the nitrate salt (**1**) confirms a head-to-head structure with a Pt...Pt separation of 2.849(1) Å. In aqueous solution, a broad lowest-energy absorption band occurs near 480 nm (ϵ 1780 M⁻¹cm⁻¹). Several observations support the assignment of this feature to the electronic transition to the predominantly singlet MLCT[$d\sigma^* \rightarrow \pi^*$] state.

In contrast to **1**, the $Pt(bpy)(MeT)_2$ monomer is yellow with lowest-energy absorption features at much shorter wavelengths: 360 (ϵ 1850 M⁻¹cm⁻¹) and 386(sh) nm (ϵ 1100 M⁻¹cm⁻¹) (Figure 5.4a). In analogy to studies of other $Pt(bpy)X_2$ complexes, these features arise from MLCT transitions.⁴⁶ Dimers lacking ancillary diimine ligands also are typically yellow (*e.g.*, head-to-head $[(NH_3)_2Pt(\mu\text{-MeT})_2Pt(NH_3)_2](NO_3)_2$, Pt...Pt 2.927(1) Å).^{16,19} Thus, the low-energy band in the spectrum of the bipyridyl dimer cannot be entirely explained by the metal-metal interaction. In fact, the singlet and triplet $d\sigma^* \rightarrow p\sigma$ transitions observed for $Pt_2(P_2O_5H_2)_4^{4-}$ occur at shorter wavelengths (Pt...Pt, 2.93 Å; $^1A_{1g} \rightarrow ^1A_{2u}$, 367, 3.45×10^4 ; $^1A_{1g} \rightarrow ^3A_{2u}$, 452 nm, 1.1×10^2 cm⁻¹M⁻¹).⁴⁷ These observations provide strong evidence for the involvement of the π^* level of the bipyridyl ligand in the lowest electronic transition of **1**. This $d\sigma^* \rightarrow \pi^*$ absorption band is considerably weaker than the pure spin-allowed $d\sigma^* \rightarrow p\sigma$ transition of $Pt_2(P_2O_5H_2)_4^{4-}$. This is, at least in part, attributable to the decreased p_z character in the LUMO. In fact, the intensity is similar to that of the lowest MLCT transitions of $Pt(bpy)X_2$ monomers. A similar band has been observed in the absorption spectra of binuclear platinum(II) terpyridyl complexes; for example, the arginine-bridged dimer (Pt...Pt, 2.998(2) Å) exhibits a lowest-energy band at 488 nm, 3700 cm⁻¹M⁻¹.⁴⁸ The slightly increased intensity in the spectrum of the terpyridyl complexes is consistent with the increased p_z - π^* mixing that has been suggested for Pt(II) terpyridyl complexes.^{49,50} We also observe

Figure 5.4 (a) Absorption spectra of $[(\text{bpy})\text{Pt}(\mu\text{-MeT})_2\text{Pt}(\text{bpy})](\text{NO}_3)_2 \cdot 3(\text{H}_2\text{O})$ (**1**) (solid line) and $\text{Pt}(\text{bpy})(\text{MeT})_2$ (dashed line) in water. (b) Absorption spectra of $[(\text{bpy})\text{Pt}(\mu\text{-pyS})_2\text{Pt}(\text{bpy})](\text{SO}_4)$ (**2b**) in water (solid line, 0.05 mM; dashed line, 0.5 mM). Inset shows temperature dependence of absorption spectrum (10-65° C).

(a)



(b)

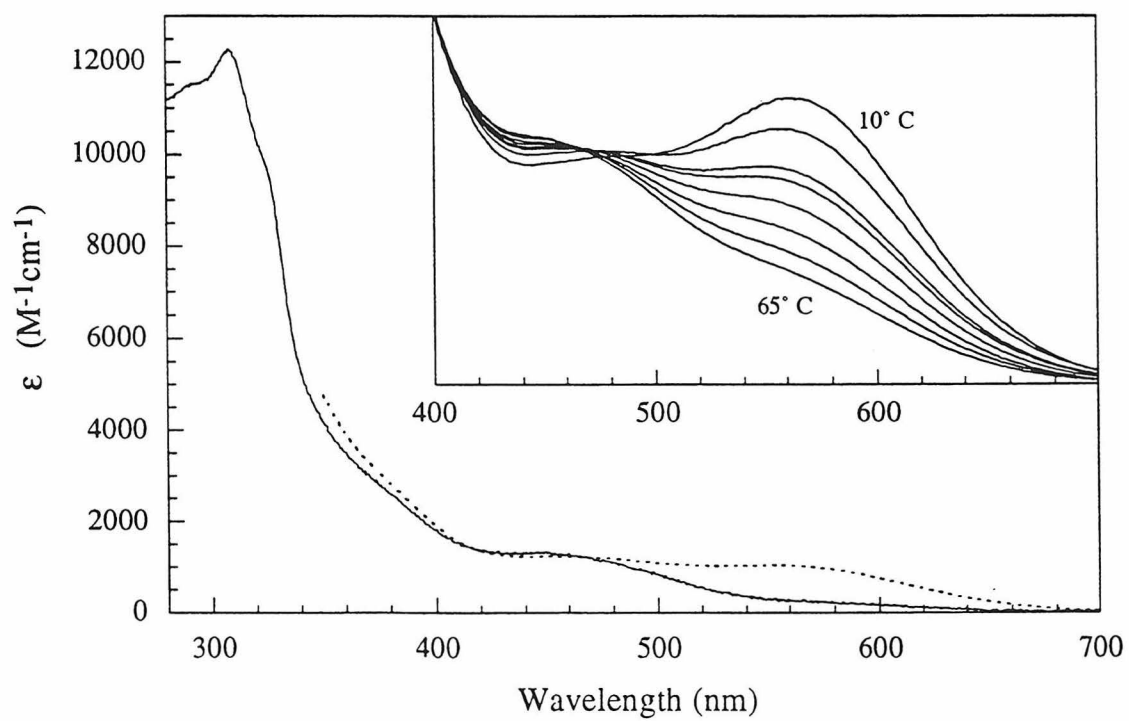


Figure 5.5 ^1H NMR spectra of $[(\text{bpy})\text{Pt}(\mu\text{-pyS})_2\text{Pt}(\text{bpy})](\text{PF}_6)_2$ (**3b**) in CD_3CN (a) before and (b) after heating for 2 hours at 50°C .

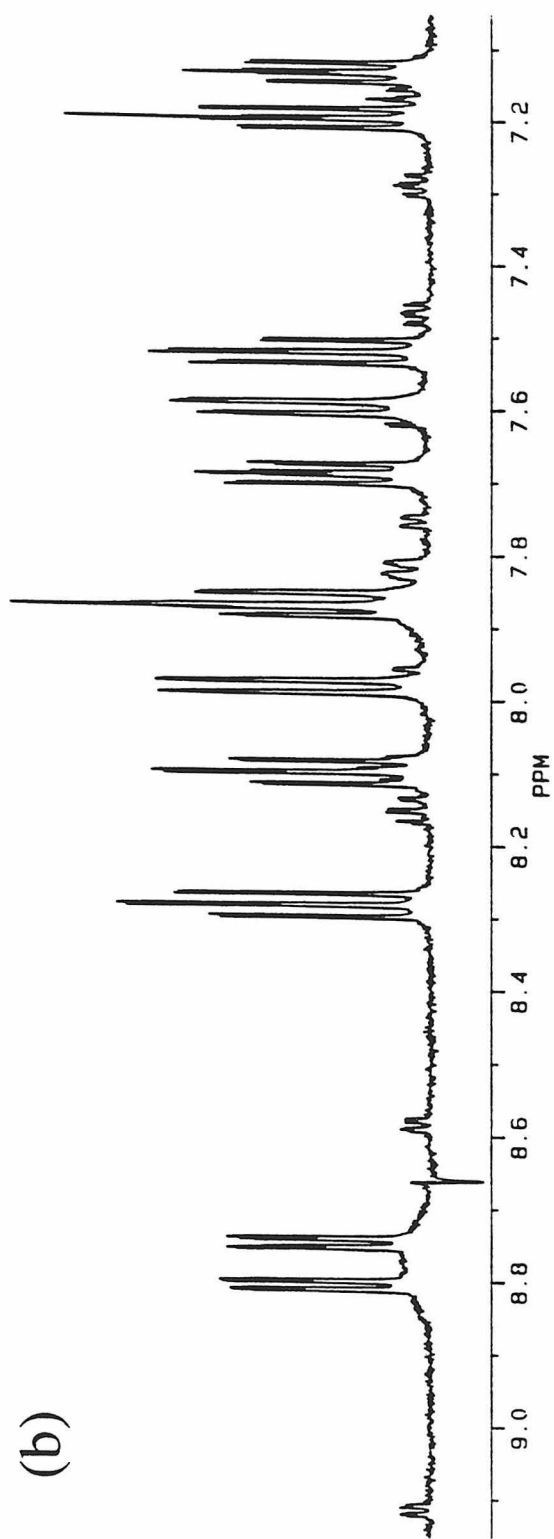
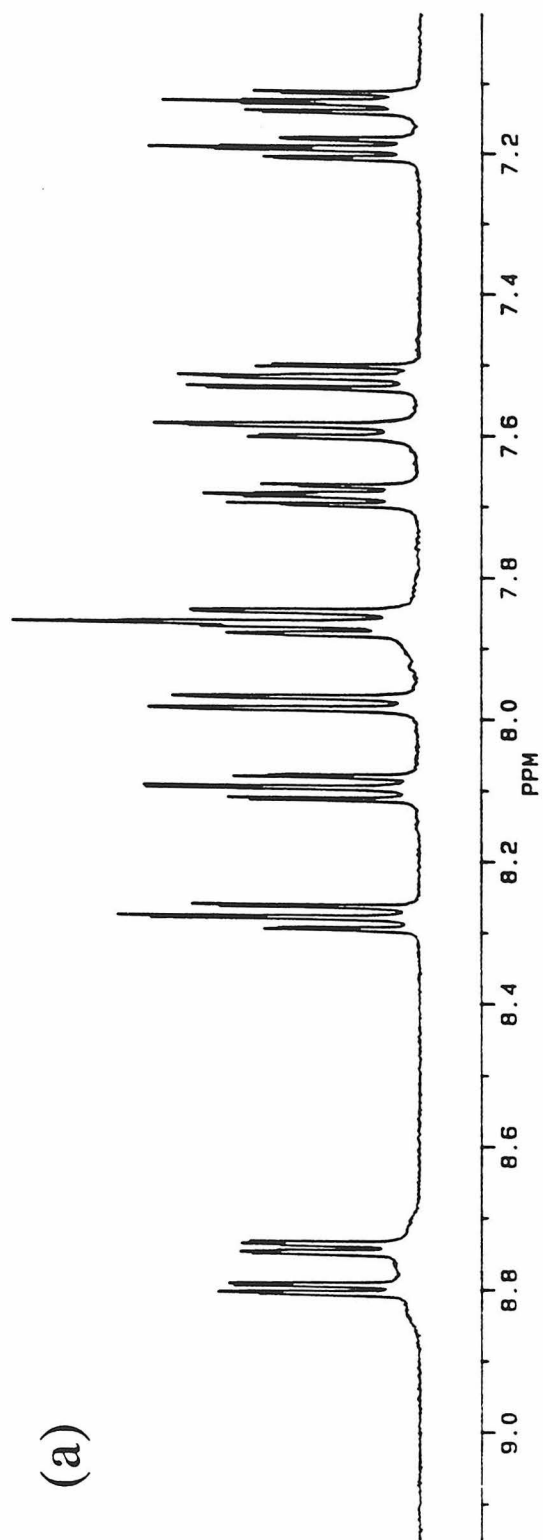
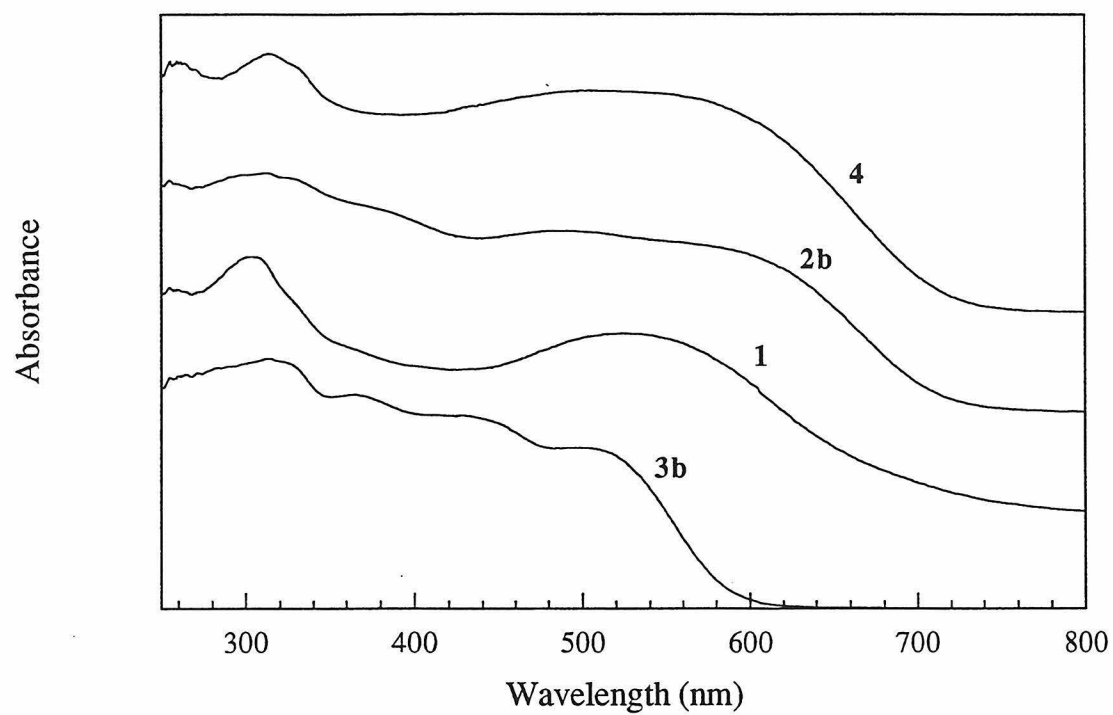
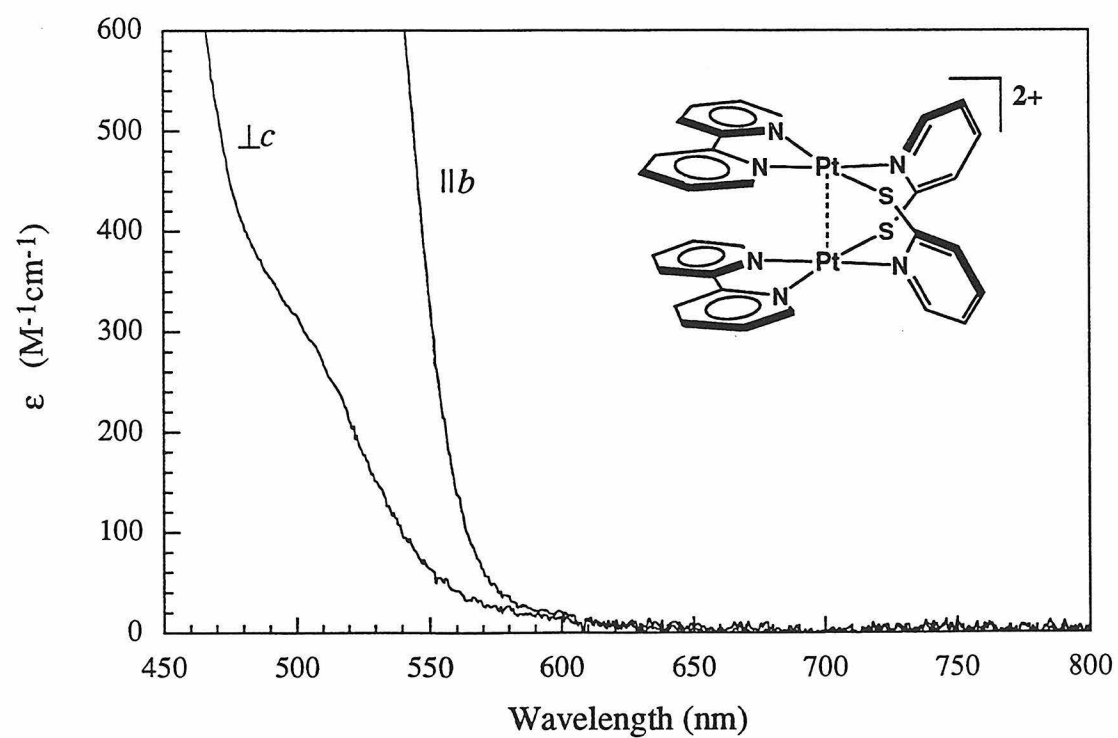


Figure 5.6 (a) Diffuse reflectance data displayed as absorption spectra for $[(bpy)Pt(\mu\text{-MeT})_2Pt(bpy)](NO_3)_2 \cdot 3(H_2O)$ (**1**), $[(bpy)Pt(\mu\text{-pyS})_2Pt(bpy)](PF_6)_2$ (**3b**), $[(bpy)Pt(\mu\text{-pyS})_2Pt(bpy)](SO_4)$ (**2b**), and $[(bpy)Pt(\mu\text{-meimidS})_2Pt(bpy)](NO_3)_2$ (**4**). Spectra are offset for purposes of display. (b) Single-crystal polarized absorption spectra for $[(bpy)Pt(\mu\text{-pyS})_2Pt(bpy)](PF_6)_2$ (**3b**). Spectra were measured perpendicular to the $[101]$ plane. The symbols $\parallel$ and $\perp$ refer to polarization parallel and perpendicular to the b axis, respectively. The Pt...Pt vector is approximately parallel to b .

(a)



(b)



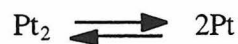
three shoulders near 395, 425 and 455 nm ($\Delta\nu$ 1800 and 1550 cm^{-1}) that may correspond to ${}^3\pi\rightarrow\pi^*$ or $d\sigma^*\rightarrow\pi^*$ vibronic structure.

2. Mercaptopyridinate Dimers

The solution chemistry of the mercaptopyridinate dimers is not fully understood. Our observations suggest the existence of several different isomers. We have found that a mixture of products is obtained using the synthetic strategies for either head-to-tail or head-to-head dimers. Originally, crystals of the head-to-tail isomer **3a** were grown from the crude reaction product. Later it was discovered that an orange product and a red-violet product could be separated by ion-exchange column. The orange product was precipitated as the PF_6^- salt from an ethanol extract; a deep orange acetonitrile solution of this material appeared to be pure by ${}^1\text{H}$ NMR (Figure 5.5a), giving rise to 12 sets of resonances from 7 to 9 ppm. Interestingly, heating this sample for 2 hours at 50° C resulted in an additional set of 12 resonances (Figure 5.5b). Crystals of *both* the red head-to-head (**2a**) and orange head-to-tail (**3b**) PF_6^- salts were discovered in the same NMR tube two weeks *after* the spectrum was collected; subsequently it was found that fractional crystallization of red acetonitrile solutions containing mixtures of the PF_6^- salts allows for separation of orange needles of **3b**. The absorption spectra of **3b** in acetonitrile obey Beer's law. The low-energy shoulder near 480 nm (ϵ 800 $\text{cm}^{-1}\text{M}^{-1}$) is most likely due to the spin-allowed $d\sigma^*\rightarrow\pi^*$ transition (Figure 5.6a). Though the $\text{Pt}(\text{bpy})(\text{pyS})_2$ monomer model complex also absorbs in this region, the lowest-energy transitions in the absorption spectra of $\text{Pt}(\text{dmbpy})(2\text{-mercaptoethanolate})$ (CH_3CN : 448 nm)⁵¹ and $\text{Pt}(\text{bpy})(\text{cysteine})^+$ (H_2O : 350 nm, 2200 $\text{cm}^{-1}\text{M}^{-1}$)⁵² occur at shorter wavelengths.

The aqueous red-violet ammonium sulfate solution obtained by chromatography showed a tendency to convert to an orange-colored solution at elevated temperatures. However, a violet product (**2b**) was obtained from an orange-colored ethanol extract by

evaporation in the absence of heat. This is most likely the sulfate salt of the head-to-head dimer; the ^1H NMR spectrum in D_2O consists of 12 sets of resonances from 7 to 9 ppm. A 0.54 mM aqueous solution of this material is deep red due to a low-energy band near 557 nm ($\epsilon \sim 1000 \text{ cm}^{-1}\text{M}^{-1}$). The energy and apparent intensity are consistent with a $\text{d}\sigma^* \rightarrow \pi^*$ transition that is somewhat red-shifted from that of **1** because of the electron-releasing properties of the thiolate ligand. It is intriguing that the absorbance does not obey Beer's law. The intensity of this band relative to higher energy features dramatically decreases at low concentration (Figure 5.4b). Similar behavior is observed with increasing temperature (Figure 5.4b). These observations are entirely consistent with an oligomerization process, such as an equilibrium involving a dimer and a monomer:



In fact, the pyS ligand is known to bind Pt monomers in a chelating geometry.^{53,54} Moreover, reports from the Jensen^{44,45,55,56} and Nakamura⁵⁷ laboratories indicate that palladium(II) mercaptopyridinate dimers often exhibit complex equilibria in solution. For example, from variable-temperature NMR studies of $\text{Cl}(\text{PMe}_2\text{Ph})\text{Pd}(\mu\text{-pyS})_2\text{PdCl}(\text{PMe}_2\text{Ph})$, values of $\Delta H = 46 \pm 2 \text{ kJ/mole}$ and $\Delta S = 109 \pm 10 \text{ J/mole}$ were calculated for the dimer-monomer interconversion.⁴⁴ While we have not fully examined the behavior of the platinum(II) bipyridyl dimers, it appears that similar processes occur in solution. However, the situation is likely to be somewhat complicated by our use of coordinating solvents. Interestingly, the absorption spectra of the 2-mercapto-1-methylimidazolate bridged dimer (**4**) show a similar concentration dependence (λ_{max} , 541 nm; absorbance, $[\text{Pt}_2]$: 0.97, 0.45 mM; 0.05, 0.045 mM), though Jensen and co-workers^{55,56} have suggested that palladium dimers with meimidS bridging ligands are stable to dissociation because the geometry of the meimidS ligand is unfavorable for chelation.

In summary, our observations suggest that in acetonitrile solution the head-to-head and head-to-tail forms of $[(\text{bpy})\text{Pt}(\mu\text{-pyS})_2\text{Pt}(\text{bpy})]^{2+}$ interconvert at elevated temperature. In aqueous solution, the barrier to interconversion may be lower. Nevertheless, it seems the two species can be separated by chromatography. The red head-to-head species shows concentration dependent behavior that is consistent with a dimer-monomer interconversion, where the $d\sigma^* \rightarrow \pi^*$ transition at 557 nm is a spectroscopic marker for the dimer. It appears that this interconversion does not involve formation of the head-to-tail adduct; however, the details of this mechanism are not known. We also note that the $d\sigma^* \rightarrow \pi^*$ transition in the orange head-to-tail adduct is shifted to higher energy of the head-to-head dimer, suggesting that the Pt centers in the head-to-tail dications are more weakly interacting on average; indeed, the structures of **3a** and **3b** suggest that there is a low barrier to perturbing the Pt...Pt separation.

3. Solid-State Studies

Diffuse reflectance spectra of several platinum(II) bipyridyl dimers are shown in Figure 5.6a. The head-to-head MeT-bridged complex (**1**) exhibits a broad absorption band centered at 525 nm; the fact that the maximum is shifted 1800 cm^{-1} to lower energy of the $d\sigma^* \rightarrow \pi^*$ transition observed in solution may indicate that the Pt...Pt separation is somewhat longer on average in solution than in the crystal. Low-energy broad shoulders also are observed in the spectra of **2b** (~585 nm) and **4** (~570 nm) indicating strongly interacting Pt centers in these materials. A preliminary measurement for **2a** was obtained with the same crystal that was used in the X-ray diffraction studies; a low-energy feature near 560 nm is most likely associated with the $d\sigma^* \rightarrow \pi^*$ transition.

The diffuse reflectance spectrum of the orange head-to-tail isomer of $[\text{Pt}(\text{bpy})(\mu\text{-pyS})_2](\text{PF}_6)_2$ (**3b**) exhibits a well-resolved band at 500 nm (Figure 5.6b). This feature is modestly shifted to lower energy from the solution maximum at 480 nm. The single-crystal polarized absorption spectra suggest that this transition is strongly

polarized along the Pt...Pt direction. In the case of stacked Pt(II) diimine complexes, a low-energy $d\sigma^* \rightarrow \pi^*$ transition also is strongly polarized along the stacking axis (see Chapter 4).⁵⁸⁻⁶¹ In fact, the spectra of **3b** bear a strong qualitative resemblance to those of the linear-chain platinum diimine complexes. Interestingly, we find no evidence of an additional feature at longer wavelengths that might be attributed to a triplet component of the $d\sigma^* \rightarrow \pi^*$ transition. Thus, the band at 500 nm may, in fact, correspond to the transition to a predominantly triplet MLCT[$d\sigma^* \rightarrow \pi^*$] state; spin-orbit coupling may strongly mix the spin states as previously established for tetracyanoplatinate.⁶²⁻⁶⁴

Compounds **1-4** are luminescent in the solid state; however, we have not observed emission from room-temperature fluid solutions. The 77 K solid-state emission spectrum of the MeT-bridged dimer (**1**) exhibits a maximum near 735 nm; the narrow asymmetric profile is similar to the emission from linear-chain Pt(II) diimine complexes (Figure 5.6a). A distinct shoulder is resolved approximately 1200 cm^{-1} further to the red of the emission maximum. Vibronic structure with this spacing is diagnostic of involvement of the bipyridyl ligand in the transition.^{65,66} The emission lifetimes measured for 77 K glassy solutions of **1** and **3b** (3 and 3.5 μs , respectively) are consistent with a predominantly spin-forbidden process. In the case of the Pt(II) terpyridyl dimers, the emission lifetimes at 77 K are 1-2.5 μs , and resonance Raman spectra show the expected enhancement of terpyridyl vibrations.⁶⁷

IV. Conclusion

The spectroscopy of binuclear platinum(II) bipyridyl complexes is qualitatively similar to that of the linear-chain platinum(II) diimine complexes. The distinctive colors of these compounds are attributed to a low-energy $d\sigma^* \rightarrow \pi^*$ transition. As observed for the stacked systems, this transition is very sensitive to the nature of the metal-metal interaction. Decreasing Pt...Pt separation stabilizes the MLCT[$d\sigma^* \rightarrow \pi^*$]. Thiolate bridging ligands also tend to stabilize these states presumably as a result of

strong Pt-S mixing and inductive effects (see Chapter 6). However, we find that some binuclear complexes with 2-mercaptopyridinate and 2-mercapto-1-methylimidazolate bridging ligands are unstable in solution, apparently existing as mixture of monomers and dimers.

Unfortunately, the complexes that we have examined do not show intense emission in room-temperature fluid solution. In contrast, the $^3d\sigma^* \rightarrow p\sigma$ state of d^8 - d^8 dimers, such as $Pt_2(P_2O_5H_2)_4^{4-}$, are typically long-lived resulting in intense fluid solution emission.¹⁻³ One possible mechanism for deactivation of the $^3MLCT[d\sigma^* \rightarrow \pi^*]$ excited state involves quenching by solvent interaction at the open coordination sites. In the excited state, the Pt centers are expected to be stronger electrophiles than in the ground state. Additionally, the high-frequency ring-stretching modes of the bipyridyl ligands provide an energy sink for non-radiative decay. Thus, we conclude by suggesting that future synthetic efforts emphasize molecular rigidity and protection of the open coordination sites.

V. References and Notes

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Chapter 6

Photooxidation of Platinum(II) Bipyridyl Benzenedithiolate

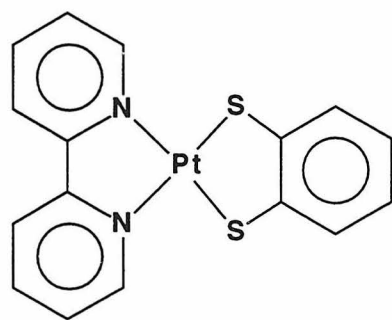
I. Introduction

An intriguing situation arises when *both* electron-donating and electron-accepting ligands are coordinated to platinum(II). Since the LUMO of platinum(II) diimine complexes is predominantly centered on the diimine ligand,¹⁻⁴ binding of strongly reducing bidentate ligands, such as dithiolates, at the ancillary metal coordination sites results in a donor-acceptor type complex. Because it is the ligands that assume the roles of donor and acceptor and the metal that acts as the bridge mediating electronic-coupling, these molecules share a converse relationship with asymmetric mixed-valence complexes (*e.g.*, $(\text{CN})_5\text{Ru}^{\text{II}}(\text{CN})\text{Ru}^{\text{III}}(\text{NH}_3)_5$)^{5,6} popularized in studies of electron transfer.⁷⁻¹⁰

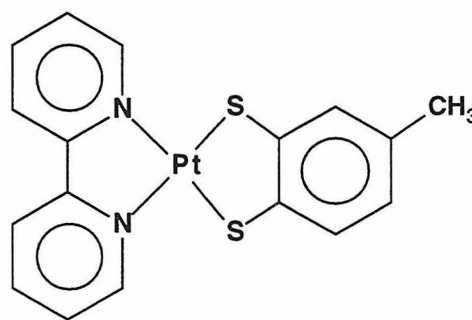
One class of these complexes, which has recently received considerable attention, are the platinum(II) diimine dithiolates. These compounds exhibit distinctly different properties from those of Pt(diimine) complexes with innocent ancillary ligands. (*e.g.*, $\text{Pt}(\text{bpy})\text{Cl}_2$; see also Chapters 2-4). Notably, they are intensely colored, often orange, red or violet, in the solid state *and* in solution. The origin of this color is an intense low-energy band in the visible absorption spectrum. In analogy to the spectroscopy of Ni(II) complexes studied by Miller and Dance,¹¹ this feature has previously been assigned to a ligand-to-ligand (dithiolate→diimine) charge-transfer (LLCT) transition.^{12,13} More recently, Eisenberg and co-workers¹⁴ have revised this assignment based on the results of extended Hückel calculations which suggest significant Pt character in the HOMO. In this description, the intense low-energy absorption band is attributed to a $^1\text{d}(\text{Pt})/\text{p}(\text{S})\pi\rightarrow\pi^*(\text{diimine})$ transition, sometimes called a charge-transfer-to-diimine transition. In accord with these assignments, the absorption band is highly solvatochromic, shifting to higher energy in more polar solvents.¹⁵

Zuleta and co-workers^{16,17} have found that platinum(II) diimine dithiolate complexes often exhibit luminescence from a long-lived triplet excited state in room-temperature fluid solution. These observations have stimulated considerable interest in the spectroscopy and photophysics of these compounds. In most cases, the LUMO is the

predominantly ligand-localized π^* orbital of the diimine; thus, the emission from complexes such as $\text{Pt}(\text{bpy})(\text{tdt})$ (λ_{max} , 735 nm; τ , 291 ns; tdt =3,4-toluenedithiolate) is believed to originate from a lowest $^3\text{d}(\text{Pt})/\text{p}(\text{S})\pi \rightarrow \pi^*(\text{diimine})$ state.¹⁵ As suggested by the long excited-state lifetime, platinum(II) diimine dithiolates are photochemically active in solution. In quenching studies, Eisenberg and co-workers have shown that these complexes undergo photoinduced electron-transfer reactions.^{15,17,18} Other photoreactions are less thoroughly characterized. For example, Vogler and Kunkely¹² have observed that $\text{Pt}(\text{bpy})(\text{tdt})$ is decomposed in chloroform solution with long-wavelength irradiation (λ_{ex} =577 nm). Similarly, Srivastava and co-workers¹⁹⁻²⁸ have observed that many platinum(II) diimine complexes with thiolate ligands, including $\text{Pt}(\text{bpy})(\text{tdt})$, sensitize the formation of singlet oxygen and decompose in air-saturated solutions. Recently, Schanze and co-workers²⁹ have elaborated on these findings. However, for the photoreactions involving alkylhalides or molecular oxygen, the photoproducts have not been fully characterized and the mechanistic details are not entirely understood.



Pt(bpy)(bdt)



Pt(bpy)(tdt)

Because of our long-standing interest in the spectroscopy of platinum(II) bipyridyl complexes, we have recently prepared $\text{Pt}(\text{bpy})(\text{bdt})$ (bdt =1,2-benzenedithiolate) with the goal of relating its spectroscopic properties to those of other complexes we have studied (see Chapters 2-4). In this chapter, we describe the spectroscopy and electronic structure of this complex. In addition, we report the results of photoreactivity studies,

including the identification of two products resulting from irradiation of oxygenated solutions of Pt(bpy)(bdt).

II. Experimental

Spectroscopic methods have previously been described in Chapter 2.

A. *Synthesis of Pt(bpy)(bdt)*

In a typical preparation, 0.338 g Pt(bpy)Cl₂ and 0.331 g AgClO₄ were warmed in 25 ml dmf (*N,N*-dimethylformamide) for 1 hr. After cooling, the AgCl was removed by filtration, and a stoichiometric amount of 1,2-benzenedithiol with two equivalents of NaOH_(aq) was added to the yellow filtrate. After several minutes, deep red needles of Pt(bpy)(bdt) formed in the intensely violet solution. Analysis (calc): C, 38.88 (39.10); 2.53 (2.46); 5.76 (5.70). Crystals suitable for structural studies were grown by slow cooling of a hot dmf solution in the dark. A crystal obtained by slow evaporation of an acetonitrile solution was found to have a similar unit cell.

Crystals of the photooxidation products were isolated from air-saturated solutions of Pt(bpy)(bdt) left standing in room light. Under these conditions, the color of the solution gradually changes from violet to yellow, and eventually colorless. Because of their lower solubilities with respect to Pt(bpy)(bdt), the photoproducts have a tendency to precipitate from solution. In the case of the monosulfinated derivative, Pt(bpy)(bdtO₂), an acetonitrile solution was allowed to evaporate to dryness leaving orange crystals and residue. The crystal of Pt(bpy)(bdt) was obtained by evaporation of a dmf solution.

B. *Electrochemistry*

All electrochemical and spectroelectrochemical measurements were made in collaboration with M. G. Hill using either a Bioanalytical Systems (BAS) Model 100 electrochemical analyzer or an EG&G Princeton Applied Research Model 173 potentiostat/galvanostat driven by a Model 175 universal programmer. Cyclic

voltammetry was performed at room temperature with a normal three-electrode configuration consisting of a highly polished glassy carbon disk working electrode and a AgCl/Ag reference electrode containing 1.0 M KCl. The working compartment of the electrochemical cell was separated from the reference compartment by a modified Luggin capillary. All three compartments contained 0.1 M solution of supporting electrolyte. Acetonitrile (Burdick and Jackson, high purity) and tetrabutylammonium hexafluorophosphate (TBAH) were used as received. Electrolyte solutions were passed through activated alumina prior to use. Electrochemical potentials reported vs. AgCl/Ag are not corrected for the junction potential. Potentials reported vs. NHE were calculated using the ferrocenium/ferrocene (Fc^+/Fc) couple as a standard. In our cell, the Fc^+/Fc couple (0.05 mM $\text{Fc}(\text{NO}_3)$) in 1.00 M KCl occurs at 0.139 V vs. SCE which corresponds to 0.340 vs. NHE. In acetonitrile solution (0.1 M TBAH), the Fc^+/Fc couple was measured at 0.42 V vs. AgCl/Ag in 1.0 M KCl. Consequently, potentials reported vs. NHE were obtained by subtracting 0.08 V from the experimentally determined potentials vs. AgCl/Ag.

Thin-layer UV-visible spectroelectrochemical measurements were performed using an optically transparent platinum working electrode.³⁰ Spectral changes were monitored by a Tracor Northern TN-6500 diode array apparatus employing a Xe arc lamp as the light source.

C. Steady-state Photooxidation Studies

The reaction rates are strongly dependent on the presence of water, and therefore, the most reproducible results were obtained using aqueous acetonitrile solutions of known water content. A 150 W tungsten light or the 514.5 nm line of an argon-ion laser attenuated to ≤ 0.01 mW were ideal excitation sources. Spectra were recorded using a Hewlett-Packard 8452A diode array spectrometer.

D. X-ray Crystallography

Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer (MoK α radiation and graphite monochromator). Intensities were corrected for Lorentz and polarization effects, as well as absorption. The intensities of three standard reflections showed no variations greater than those predicted by counting statistics. For each structure, the Pt coordinates were obtained from Patterson maps, and remaining non-hydrogen atom positions were determined from successive structure-factor, Fourier calculations. Ligand H atoms were positioned by calculation (C-H, 0.95 Å). Pertinent experimental data are collected in Table 6.1 and selected bond distances and angles are given in Table 6.2. In all cases, weights were taken as $1/\sigma^2(F_o^2)$; variances [$\sigma^2(F_o^2)$] were derived from counting statistics plus an additional term, $(0.014F_o^2)^2$; variances of the merged data were determined by propagation of e.s.d.s plus another additional term, $(0.014\langle F_o^2 \rangle)^2$. Atomic scattering factors were taken from Cromer and Waber.^{31,32} Computer programs used were those of the CRYM crystallographic computing system³³ and ORTEP II.³⁴ Full details of these structures are available from the Caltech X-ray Crystallography Facility.

In the case of Pt(bpy)(bdtO₂), the structure is disordered, and the oxygen atoms O1 and O2 that are bound to S1 refined to 90% site occupancy; atoms O3 and O4 that are bound to S2 have lower occupancy, but still apparently greater than 10%. Since the UV-visible absorption and ¹H NMR spectra are consistent with a mixture of B and Pt(bpy)(bdtO₄), we have modeled the diffraction data as a mixture of both products.³⁵ From the oxygen site occupancies, we find 84% Pt(bpy)(bdtO₂) and 14% Pt(bpy)(bdtO₄). We find no evidence for a sulfenate product (*i.e.*, sulfoxide product) in the crystal structures.

Table 6.1. Crystallographic data for Pt(bpy)(bdt), Pt(bpy)(bdt-O₂) and Pt(bpy)(bdt-O₄)·(H₂O).

	Pt(bpy)(bdt)	Pt(bpy)(bdt-O ₂) ^c	Pt(bpy)(bdt-O ₄)·H ₂ O
formula	PtC ₁₆ H ₁₂ N ₂ S ₂	PtC ₁₆ H ₁₂ N ₂ S ₂ O _{2.28}	PtC ₁₆ H ₁₄ N ₂ S ₂ O ₅
<i>M_w</i>	491.49	527.96	573.50
color	violet	orange	yellow
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>a</i> , Å	8.206(2)	8.045(2)	11.513(2)
<i>b</i> , Å	11.456(4)	14.629(3)	7.103(1)
<i>c</i> , Å	16.350(4)	13.342(4)	20.856(3)
<i>β</i> , °	103.14(2)	101.71(2)	101.64(1)
<i>V</i> , Å ³	1496.8(7)	1537.5(7)	1670.5(4))
<i>D_{calc}</i> , g/cm ³	2.18	2.28	2.28
<i>Z</i>	4	4	4
<i>μ</i> , cm ⁻¹	97.33	94.93	87.58
no. reflcns	2634	2704	2943
no. reflcns <i>F_o</i> ² >0	2469	2493	2775
no. reflcns <i>F_o</i> ² >3σ(<i>F_o</i> ²)	2087	1993	2151
no. parameters	190	228	235
GOF ^a	1.37	1.19	1.71
<i>R</i> ^b	0.033	0.034	0.055
<i>R</i> (<i>F_o</i> ² >3σ(<i>F_o</i> ²)) ^b	0.0240	0.022	0.039

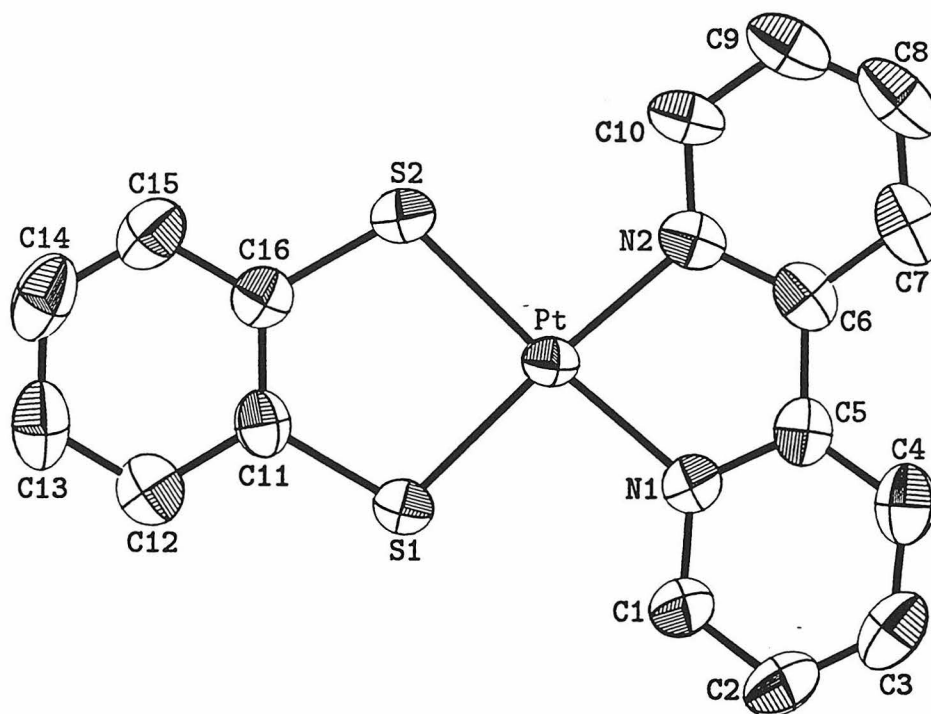
^a $\text{GOF} = \left(\sum w(F_o^2 - F_c^2)^2 / (n - p) \right)^{1/2}$ where *n* is the number of data and *p* is the number of parameters refined.

^b $R = \sum |F_o - |F_c|| / \sum |F_o|$

^c For the structure of Pt(bpy)(bdtO₂) O1 and O2 have 92% occupancy, and O3 and O4 have 22% occupancy; the crystal contains 14% Pt(bpy)(bdtO₄).

Figure 6.1 (a) *ORTEP*II³⁴ diagrams with 50% probability ellipsoids showing the geometry of the Pt(bpy)(bdt) molecule. (b) View of the crystal packing. H atoms are not shown.

(a)



(b)

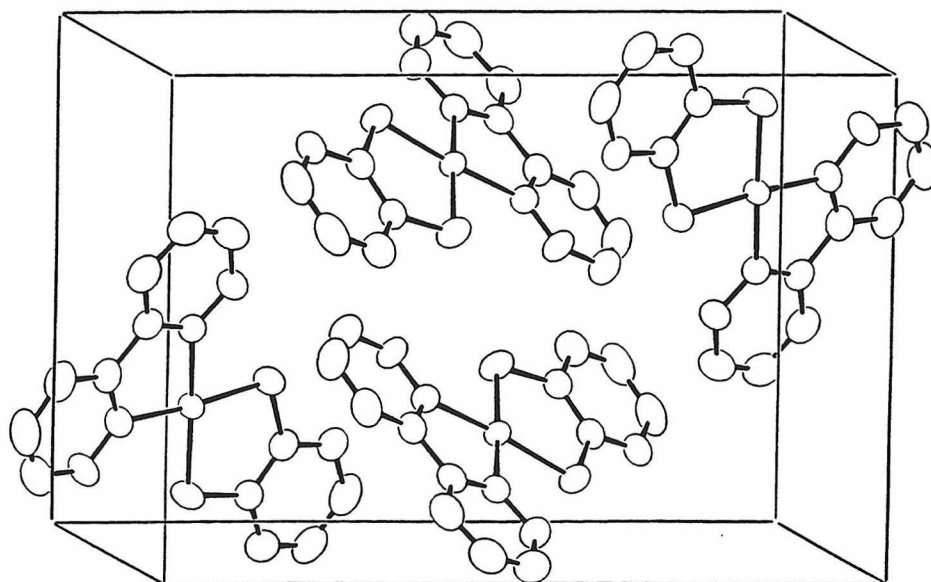


Table 6.2. Selected bond lengths (Å) and angles (°) for Pt(bpy)(bdt), Pt(bpy)(bdtO₂)^a and Pt(bpy)(bdtO₄).

	Pt(bpy)(bdt)	Pt(bpy)(bdtO ₂) ^a	Pt(bpy)(bdtO ₄)
Pt-S1	2.244 (2)	2.223 (1)	2.235 (3)
Pt-S2	2.250 (2)	2.256 (2)	2.218 (3)
Pt-N1	2.050 (4)	2.074 (4)	2.065 (8)
Pt-N2	2.049 (5)	2.075 (4)	2.076 (9)
S1-C11	1.762 (6)	1.717 (6)	1.780 (10)
S2-C16	1.759 (6)	1.747 (6)	1.781 (10)
C11-C16	1.373 (8)	1.385 (8)	1.388 (14)
N1-C5	1.348 (7)	1.354 (7)	1.352 (13)
N2-C6	1.389 (8)	1.352 (7)	1.372 (12)
C5-C6	1.464 (8)	1.468 (8)	1.505 (14)
S1-O1	—	1.460 (5)	1.462 (10)
S1-O2	—	1.442 (5)	1.430 (9)
S2-O3	—	1.272 (19)	1.455 (8)
S2-O4	—	1.605 (18)	1.467 (9)

^a For the structure of Pt(bpy)(bdtO₂) O1 and O2 have 92% occupancy, and O3 and O4 have 22% occupancy; the crystal contains 14% Pt(bpy)(bdtO₄).

III. Results and Discussion

A.. Structure of Pt(bpy)(bdt)

The molecule, including the numbering system, is drawn in Figure 6.1a and the packing is shown in Figure 6.1b; selected distances and angles are given in Table 6.1. The molecule is slightly bowed with an average deviation of 0.06(4) Å per atom for a best-fit plane defined by the positions of the atoms. Distances and angles in the ligands are normal.

The Pt-N bond lengths (2.050(4), 2.049(5) Å) are within the range of those observed for other platinum(II) diimine complexes with dithiolate (2.03-2.06 Å)³⁶⁻³⁸ and

cyanide ligands³⁹⁻⁴¹ (e.g., Pt(bpy)(CN)₂, 2.059(5) Å), but they are significantly longer than found for the red and yellow forms of Pt(bpy)Cl₂ (2.009(6) and 2.01(1) Å).⁴² The Pt-S distances (2.244(2), 2.250(2) Å) are characteristically short, suggesting a strong Pt-S interaction. The Pt-S distances are similar to those of other platinum(II) diimine dithiolates³⁸ (Pt(bpm)(mnt), 2.245(3), 2.254(2), mnt=maleonitriledithiolate, bpm=2,2'-bipyrimidine;³⁶ Pt(dmbpy)(met), 2.245(2), 2.244(2) Å, met=*cis*-1,2-dicarbomethoxyethylene-1,2-dithiolate, dmbpy=4,4'-dimethyl-2,2'-bipyridine),⁴³ but they are shorter than found for complexes with phosphine ligands (Pt(dppe)(mnt), 2.303(2) and 2.296(2) Å, dppe=1,2-bis(diphenylphosphino)ethane).^{37,43}

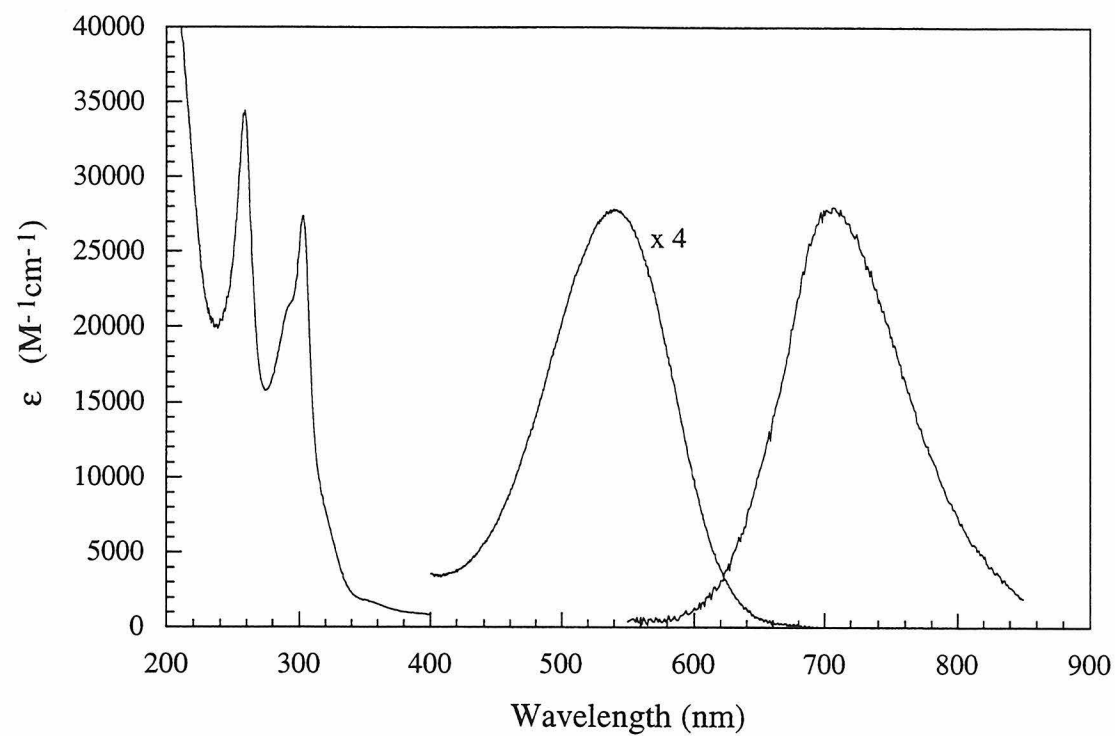
B. Electronic Structure

The absorption spectrum of Pt(bpy)(bdt) is understandably similar to spectra of Pt(diimine)(tdt) complexes (Figure 6.2a). Two solvent-insensitive, intense narrow bands are observed in the UV region (acetonitrile: 260 nm, ϵ 34500 M⁻¹cm⁻¹; 310 nm, ϵ 27400 M⁻¹cm⁻¹). In analogy to our discussion in Chapter 2, the lower energy feature is assigned to the bipyridyl localized $\pi \rightarrow \pi_1^*$ transition; the higher energy band lies very near the $\pi \rightarrow \pi_2^*$ transition observed in the spectra of other Pt(bpy)X₂ complexes (~250 nm). The high intensities of these bands indicates that transitions associated with the bdt ligand also overlap this region. At longer wavelengths, a shoulder is resolved near 350 nm (ϵ 1850); in chloroform, the shoulder shifts to ~363 nm. The energy, intensity and solvent sensitivity are consistent with a ¹MLCT[d $\rightarrow$ $\pi^*(bpy)$] transition. It is striking that this band occurs within the 330-450 nm range where we have observed the d π (Pt) $\rightarrow$ $\pi^*(diimine)$ transition in the spectra of Pt(diimine)X₂ complexes with innocent ligands, that is, ligands that do not participate in the observed electronic transitions.

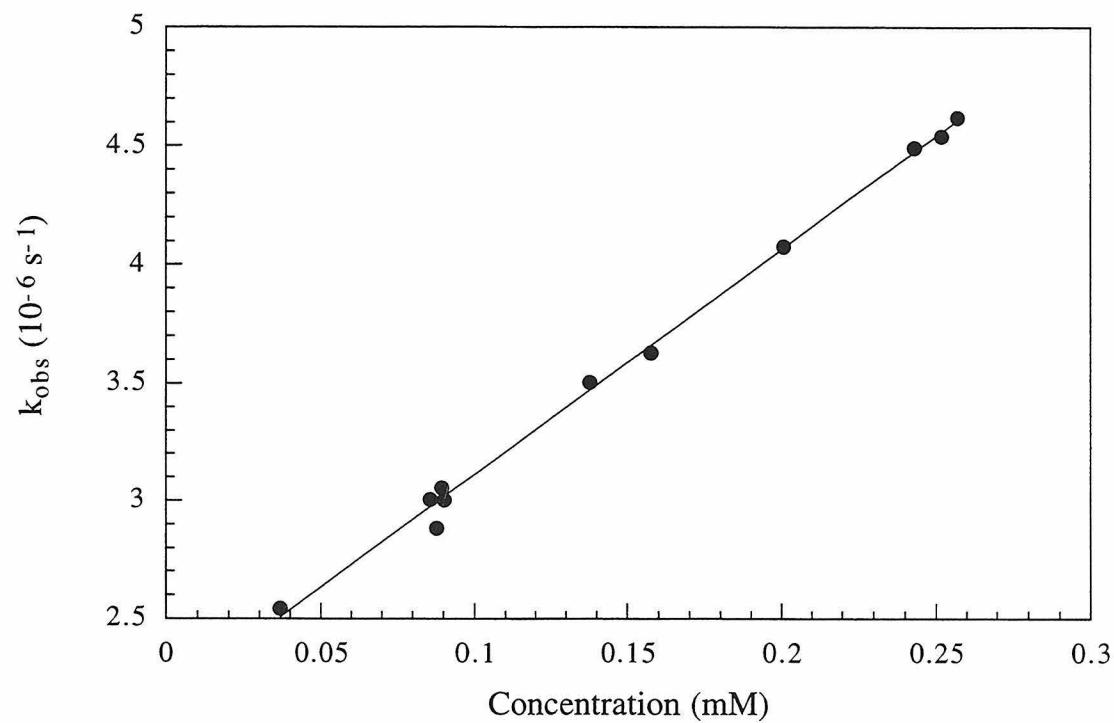
A very broad and solvent sensitive band occurs at longer wavelengths (acetonitrile λ_{max} , Å (ϵ , M⁻¹cm⁻¹), 542 (6960); dmf, 557 (7080); chloroform, 600).

Figure 6.2 (a) Absorption and uncorrected emission spectra for Pt(bpy)(bdt) in acetonitrile. (The corrected emission maximum occurs near 750 nm.) (b) Stern-Volmer analysis of self-quenching of the Pt(bpy)(bdt) excited state. The rate of excited-state decay (k_{obs}) is shown as a function of the concentration of Pt(bpy)(bdt) in acetonitrile. From the linear fit, the intrinsic lifetime (τ_0) is 460 ns, and the quenching rate constant (k_q) is $9.5 \times 10^9 \text{ s}^{-1}$.

(a)



(b)



The band shifts dramatically to lower energy in less polar solvents suggesting considerable charge-transfer character. We emphasize that this transition occurs $\sim 7000\text{ cm}^{-1}$ to lower energy from the lowest spin-allowed MLCT transition found in the absorption spectra of $\text{Pt}(\text{bpy})\text{X}_2$ complexes with innocent ligands, suggesting the special role of the dithiolate ligand. On the other hand, in the solid-state diffuse reflectance spectrum this feature exhibits vibronic structure with spacings ($1100\text{--}1600\text{ cm}^{-1}$) that are diagnostic of bipyridyl participation.^{44,45} A similar band has been observed in the spectra of numerous platinum(II) dithiolate complexes and has been assigned to a LLCT involving transfer of electron density from the dithiolate ligand to the diimine ligand. Thus, the large negative solvatochromism is attributable to a polar ground state and a nonpolar excited state.¹⁵ Resonance Raman studies of related nickel and palladium compounds also support this assignment.⁴⁶ Recently, Eisenberg and co-workers¹⁴ have suggested that the transition is more accurately described as a $^1\text{d}(\text{Pt})/\text{p}(\text{S})\pi\rightarrow\pi^*(\text{diimine})$ transition. Indeed, the importance of the metal is suggested by the energies and intensities of this band in the spectra of related complexes:

	λ_{max}	$\epsilon\text{ (M}^{-1}\text{cm}^{-1}\text{)}$
$\text{Pt}(\text{bpy})(\text{tdt}), \text{dmf}^{19}$	568	7400
$\text{Pt}(\text{bpy})(\text{tdt}), \text{dmf}^{19}$	498	1600
$\text{Zn}(\text{bpy})(\text{tdt}), \text{CHCl}_3^{47}$	465	65

The nearly 4000 cm^{-1} blue-shift and 90% loss in intensity along the Pd, Pt, Zn series suggests significant differences in metal contribution. For example, the pseudo-tetrahedral geometry of the Zn complex severely attenuates the electronic coupling.⁴⁸ Thus, the participation of the metal in the coupling interaction is firmly established, and consequently, we describe this transition as a metal-mixed LLCT.

Like many platinum(II) diimine dithiolate complexes, Pt(bpy)(bdt) is luminescent in room-temperature fluid solution (Figure 6.2a). What is unusual, however, is that the excited-state lifetime is concentration dependent (Figure 6.2b), so that the lifetime decreases as the concentration of complex in solution is increased. This behavior is characteristic of a self-quenching process. A Stern-Volmer analysis indicates that the intrinsic lifetime of the excited state is 460 ns in acetonitrile and the quenching rate (k_q , $9.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) is near the diffusion limit; for chloroform solution, the intrinsic lifetime is 560 ns (k_q , $4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). It seems likely that the self-quenching reaction involves formation of an excimer; as reported for other platinum(II) diimine systems.^{49,50} However, this species and its corresponding emission have not been directly observed; we note that excimer emission is likely to occur at wavelengths outside the detection limits of our instrument ($>850 \text{ nm}$). It is intriguing that Pt(bpy)(tdt) and other tdt complexes do not exhibit this self-quenching behavior. It seems possible that the methyl group on tdt reduces the association constant. Alternatively, this behavior may have gone unnoticed in earlier work.

The emission band overlaps the low-energy tail of the absorption band and has a similar solvent dependence. In addition, a distinct shoulder is resolved in the solid-state emission spectrum shifted 1040 cm^{-1} to lower energy of the parent peak (730 nm), again indicating the involvement of the bipyridyl ligand in the electronic transition. Moreover, the long excited-state lifetime indicates a spin-forbidden process. In analogy to studies of related complexes,^{12,14-18,37,51-53} the emission is proposed to originate from a metal-mixed LLCT state with triplet character. Electrochemical measurements also are consistent with this assignment (*vide infra*).

The nature of the metal-mixed LLCT state in these complexes has been discussed in considerable detail,¹³⁻¹⁵ and we neither dispute nor duplicate those comments here. However, we do offer a somewhat different perspective on the LLCT transitions than has been given elsewhere. It is clear that the metal-mixed LLCT absorption in these

complexes has considerable singlet character and that the emission has considerable triplet character. Although a corresponding triplet absorption feature has not been resolved in the spectra of platinum(II) diimine dithiolate complexes, they are believed to be buried in the low-energy tail of the absorption band.¹⁵ From the overlap of the emission spectrum with the absorption spectrum, it is apparent that the gap between these singlet and triplet states is small ($\sim 1000\text{ cm}^{-1}$). In fact, it appears that this gap is smaller than found for splitting of unimolecular singlet-triplet MLCT states of platinum diimine complexes ($3000\text{--}4000\text{ cm}^{-1}$); this situation is consistent with spin-orbit coupling with the Pt, as well as an excited state involving large spatial separation of the unpaired electrons - as expected for the LLCT state. Alternatively, the intense absorption band may correspond to the transition to a strongly spin-orbit coupled triplet LLCT state, and the emission originates from a more weakly coupled spin-orbit state. This situation is similar to that observed for the MLCT transitions of $\text{Pt}(\text{CN})_4^{2-}$.⁵⁴⁻⁵⁶

Thus, we have a problem involving coupling of orbitals of three units: the dithiolate, the metal, and the diimine. From the perspective of perturbation theory, this may be approached in several different ways, each converging on the observed situation. For example, Eisenberg's $d(\text{Pt})/p(\text{S})\pi \rightarrow \pi^*(\text{diimine})$ ^{14,15} description emphasizes the strong Pt-S mixing in the HOMO; given the well-established importance of $\pi^*(\text{diimine})$ - $p_z(\text{Pt})$ mixing in $\text{Pt}(\text{diimine})\text{X}_2$ complexes,³ we can assume that this description also implicitly accounts for the Pt-diimine mixing in the LUMO. An equally valid description considers the role of the Pt in coupling a HOMO isolated on the dithiolate and a LUMO localized on the diimine. In either case, the corresponding LLCT transition is strongly coupled to the intense $d \rightarrow p$ transitions of platinum.

If the Pt is regarded as the bridge facilitating electronic coupling between the HOMO and LUMO, the excited state is approximated as an oxidized dithiolate ligand and a reduced diimine. Therefore, the decay of this excited state involves transfer of an electron from the diimine to the dithiolate. This naturally leads us to interpret the non-

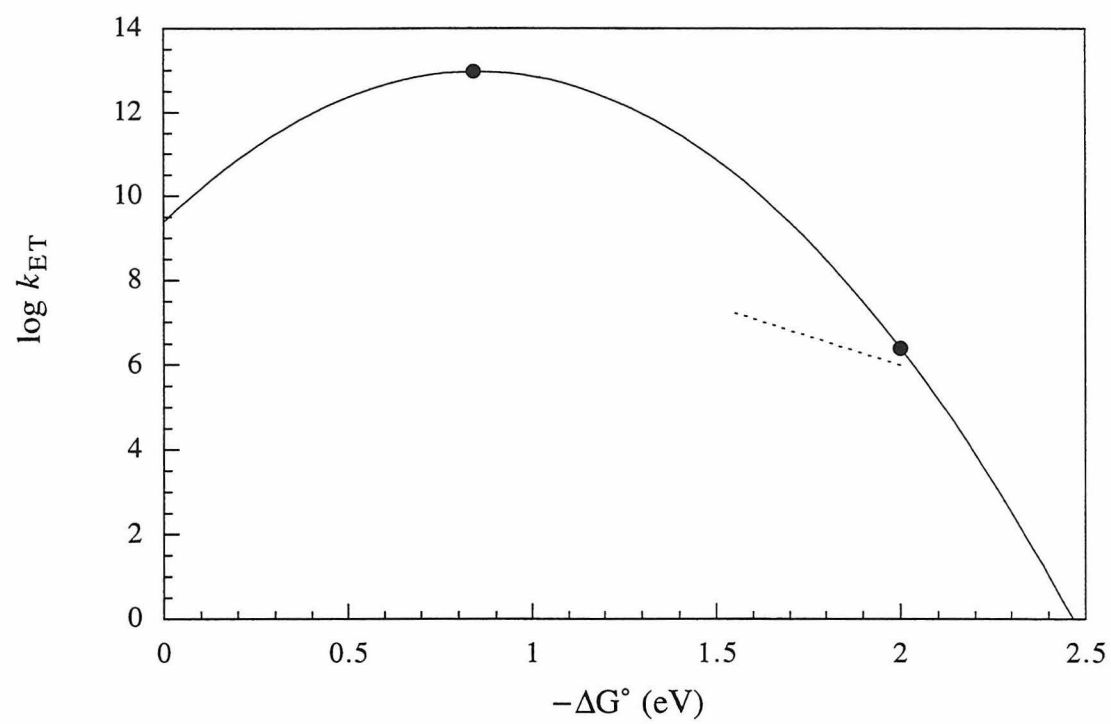
radiative excited-state decay process in terms of semi-classical electron-transfer (ET) theory⁵⁷ which describes the rate (k_{ET}) for a nonadiabatic electron transfer reaction between a rigidly held donor and acceptor:

$$k_{\text{ET}} = \frac{2H_{\text{AB}}^2}{h} \sqrt{\frac{\pi^3}{\lambda RT}} \exp\left[-\frac{(\lambda + \Delta G^0)^2}{4\lambda RT}\right] \quad (6.1)$$

where h is Planck's constant, R is the gas constant, and T is the temperature. Thus, the rate is given as a function of the electronic tunneling matrix element (H_{AB}), the reaction driving force ($-\Delta G^0$), and the reorganization energy (λ). For excited-state decay, the reaction is highly inverted. The electron transfer rate is approximated by the emission decay rate ($1/\tau$),⁵⁸ and the driving force is given by the $E_{0,0}$ of the electronic transition. Assuming k_{ET} is 10^{-13} s^{-1} in the adiabatic limit (with $-\Delta G^0 = \lambda$), we find H_{AB} and λ to be 185 cm^{-1} and 0.85 eV , respectively (Figure 6.3a). The relatively large estimated excited-state reorganization energy^{59,60} is remarkably similar to the value (0.83 eV) obtained from a bandshape analysis assuming λ is dominated by outer-sphere reorganization energetics;⁶¹ this assumption is consistent with a highly charge-separated excited state. Recently, a series of $\text{Pt}(\text{diimine})(\text{tdt})^{15}$ complexes have been shown to obey the Energy Gap Law⁶² where $\ln(k_{\text{ET}})$ shows a linear dependence on $E_{0,0}$ for the LLCT ($= -\Delta G^0$), where k_{ET} is given by the non-radiative decay rate. This result is qualitatively consistent with our ET analysis since the dependence of $\ln(k_{\text{ET}})$ on driving force, though formally parabolic by equation 6.1, is predicted to be approximately linear at high driving force (*i.e.*, deep in the inverted region). However, for quantitative agreement, the electron-transfer description requires refinement; the values of $\ln(k_{\text{ET}})$ for the series of tdt complexes show a more modest dependence on $E_{0,0}$ suggesting a somewhat weaker coupling than predicted in the adiabatic limit, as well as significant contributions from quantum modes (see Figure 6.3a and caption).

Figure 6.3 (a) Treatment of the non-radiative excited-state decay of Pt(bpy)(bdt) in terms of semi-classical ET theory (equation 6.1).⁵⁷ The logarithm of k_{ET} is plotted as a function of driving force. The data point at the top of the parabola is based on an estimate of k_{ET} (10^{13} s^{-1}) when $-\Delta G^\circ = \lambda$ (reorganization energy) - that is, the adiabatic limit; the other point is determined from the emission lifetime in acetonitrile solution. The line shows the Energy Gap Law behavior (*i.e.*, linear dependence of k_{ET} on $-\Delta G^\circ$) for a series of Pt(diimine)(tdt) complexes;¹⁵ our single lifetime measurement agrees well with these results. However, the semi-classical ET treatment gives a poor fit to these data, and thus, provides insight into the nature of the decay process. For a reasonable value of λ , k_{ET} when $-\Delta G^\circ = \lambda$ must be considerably less than the value at the adiabatic limit. This implies that there is a barrier to electron transfer, such as a spin restriction for the singlet-triplet crossover; this interpretation is entirely consistent with the apparent spin-barrier to the radiative transition. Additionally, the weaker dependence of k_{ET} on $-\Delta G^\circ$ at high driving force is often observed in ET studies and is usually regarded as an indication of nuclear tunneling.⁷⁻⁹ Coupling between the low-lying vibrational levels of the excited state with the high-lying vibrational levels of the ground electronic state accelerates the ET reaction by effectively lowering the reaction barrier. From overlap considerations,⁶² high frequency vibrational modes, such as the aromatic ring modes ($1000\text{-}1500 \text{ cm}^{-1}$) observed as vibronic structure in emission spectra, are likely to be the best energy-accepting modes. (b) Modified Latimer diagram for Pt(bpy)(bdt) with potentials reported vs. NHE.

(a)



(b)

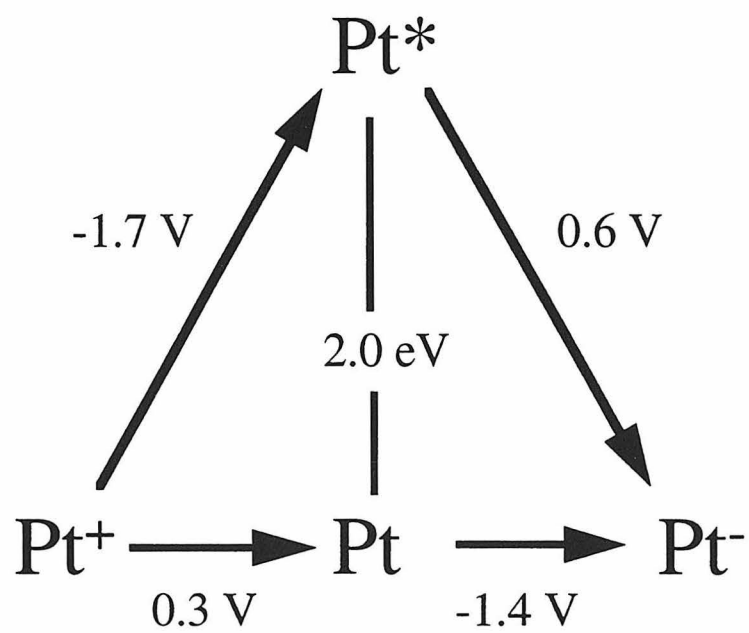
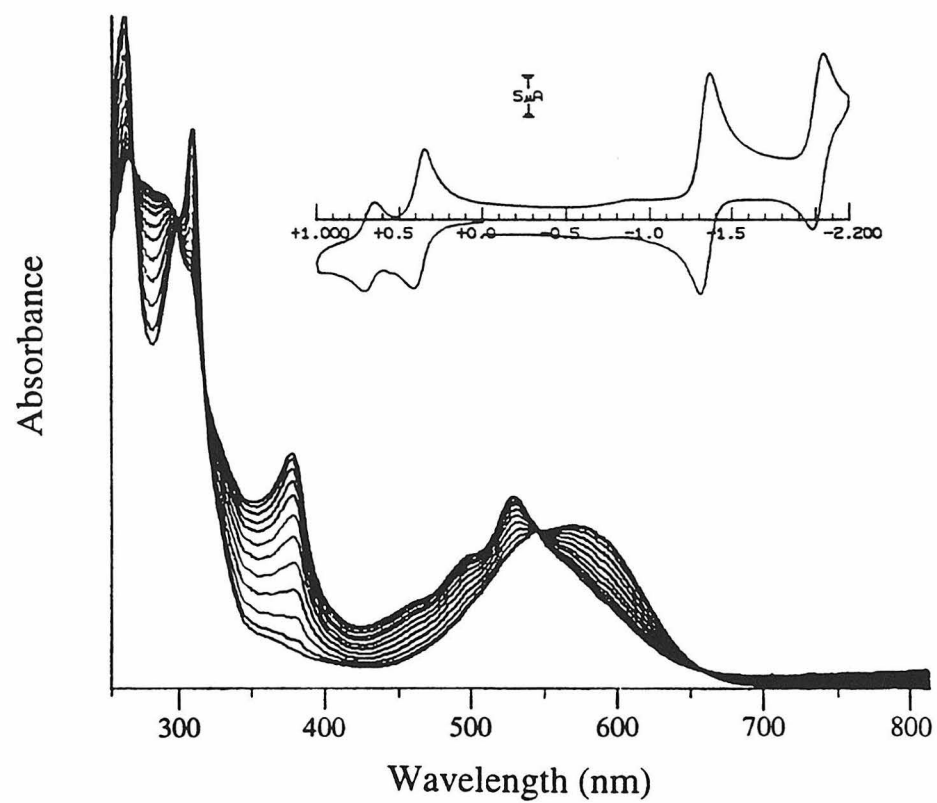
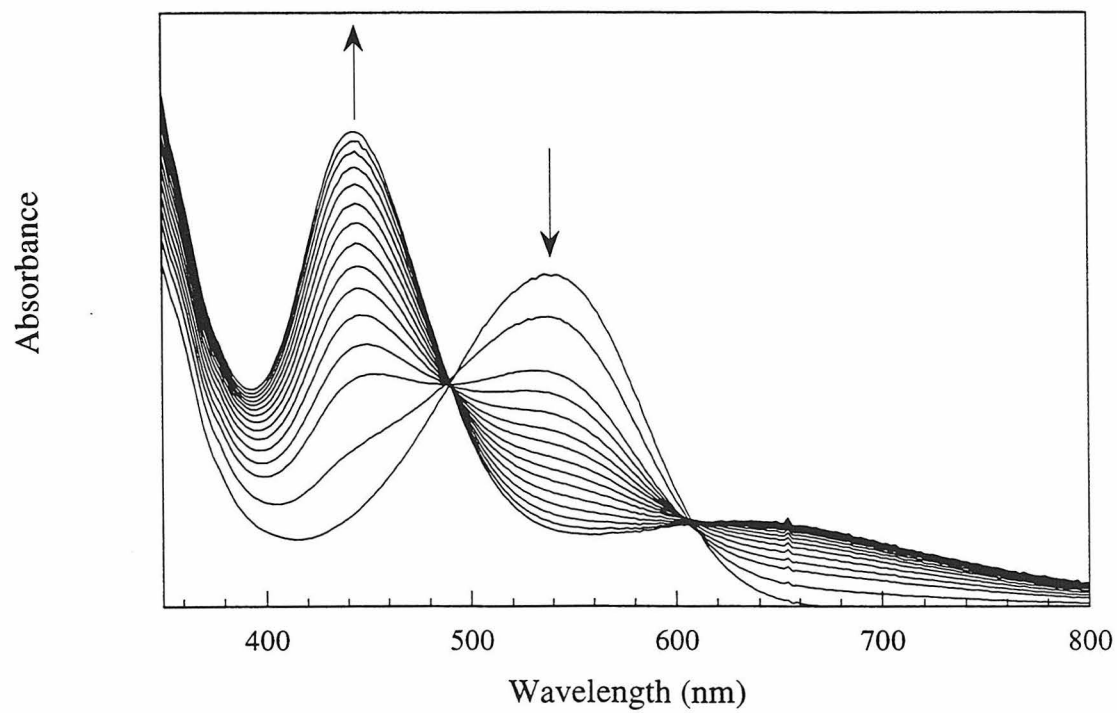


Figure 6.4 (a) Absorption spectra recorded during the reduction of Pt(bpy)(bdt) in 0.1 M TBAH /acetonitrile during a sweep past the $E_{0/-0}$ couple. The extinction coefficient for the band near 370 nm in the spectrum of the reduced complex is $10^4 \text{ M}^{-1}\text{cm}^{-1}$. Inset shows the corresponding cyclic voltammogram (100 mV/s scan rate; V vs. AgCl/Ag). (b) Absorption spectra recorded during addition of one equivalent of Ce^{4+} (2.5 mM $\text{Ce}(\text{NO}_3)_4$ in H_2O) to an acetonitrile solution of Pt(bpy)(bdt). Arrows indicate spectral changes during addition of oxidant.

(a)



(b)



C. Electrochemistry

The cyclic voltammogram of Pt(bpy)(bdt) in acetonitrile (0.1 M TBAH) is shown in Figure 6.4a. The complex exhibits two chemically reversible half-electron oxidations at 0.40 and 0.70 V and a one-electron reduction at -1.31 V vs. AgCl/Ag in 1.0 M KCl. A second reduction at -1.99 V is irreversible. The two-half electron oxidations are not fully understood, though they are consistent with dimer formation. Unfortunately, electrode surface adsorption prevented complete characterization of these processes. With these potentials and the $E_{0,0}$ estimated from the absorption and emission spectra, the modified Latimer diagram in Figure 6.3b was constructed.^{58,63} It is evident that in the excited state, Pt(bpy)(bdt) is a powerful reductant and moderate oxidant.

The first reduction process occurs at potentials characteristic of platinum(II) bipyridyl dithiolate complexes and is consistent with a bipyridyl ligand reduction.¹⁵ These couples tend to be more negative than found for other platinum bipyridyl compounds (*e.g.*, [Pt(bpy)(pyridine)₂](PF₆)₂, -0.88 V vs. AgCl(1.0 M KCl)/Ag, 0.1 M TBAH dmf;³ Pt(bpy)Cl₂, -1.06 V vs. AgCl/Ag, 0.1 M NBu₄BF₄ dmf).^{4,64} Nevertheless, the reduction of Pt(bpy)(bdt) is slightly more positive than that of Ru(bpy)₃²⁺ (-1.36 V vs. AgCl(1.0 M KCl)/Ag); this effect has been attributed to mixing of the bipyridyl π^* orbitals with the Pt(II) orbitals.^{3,4,64} The spectrum of the reduced species exhibits features characteristic of bpy anion radical, confirming that the LUMO is predominantly ligand-centered (Figure 6.4a).^{2,4,64}

The reversible low oxidation couple suggests a largely dithiolate localized process. Platinum(III) complexes are rarely stable due to nucleophilic attack at the axial coordination sites.⁶⁵ Moreover, even with strongly electron-donating and bulky mesityl ligands, Pt(bpy)(mesityl)₂ is reversibly oxidized to the Pt(III) species at ~0.9 V vs. AgCl/Ag (0.45 V vs. Fc/Fc⁺, 0.1 M TBAH tetrahydrofuran).^{2,66} The difference in the oxidation and reduction potentials (1.7 V) is slightly smaller than the $E_{0,0}$ (2.0 V) for the metal-mixed LLCT transition, supporting the notion of a highly charge-separated excited

state. If the second half-electron oxidation is taken as the oxidation potential, the difference becomes 1.9 V.

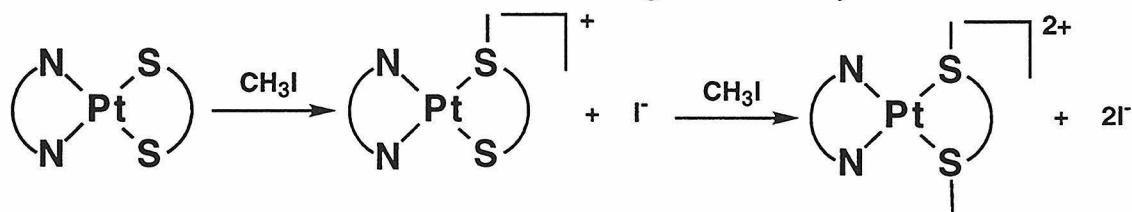
The spectrum of the one-electron oxidized species was obtained by spectroelectrochemistry, as well as chemical titration (Figure 6.4b). The spectra are similar and no evidence of oligomerization was observed. The frozen solution EPR spectrum (1:1 Ce(IV):Pt(bpy)(bdt)) of the oxidized complex gave a g value of 2.0035(2); the signal was slightly broad (80 G), though no anisotropy was observed. The similarity of the g value to the free-electron value of 2.0023 and the absence of anisotropy or fine structure are consistent with a predominantly dithiolate-centered oxidation.

E. Reactivity Toward Alkyl Halides

The reaction of Pt(bpy)(bdt) with excess CH₃I in room temperature dmf solution under argon is readily monitored by absorption spectroscopy (Figure 6.5). Initially, the solution changes in color from violet to yellow as the LLCT band decays giving rise to a new feature near 458 nm. Early in the course of the reaction, the absorbances at 384 and 478 nm do not change (pseudo-isosbestic points); however, at longer times spectral changes occur at these wavelengths, and a new band emerges at 386 nm as the 458 nm band decays. This behavior suggests the occurrence of more than one chemical process. Kinetic analysis of the absorption spectral changes indicate that these data are well-modeled as an A→B→C type process. Similar behavior is observed for acetonitrile solutions.

Methylation of the coordinated sulfur atom of metal thiolate complexes by alkyl halides is well known and has been the focus of several studies.⁶⁷⁻⁷⁰ For example, red Ni(mercaptoquinolate)₂ reacts with methyl iodide under mild conditions to form the yellow bis(thioether) complex, Ni(S-methyl-8-mercaptoquinoline)₂.⁶⁷ Faxlur-Rahman and Verkade⁷¹ have reported that reaction of one equivalent of CH₃I with Pt(depe)(bdt) (depe=1,2-bis(diethylphosphino)ethane) results in the addition of a methyl group to one

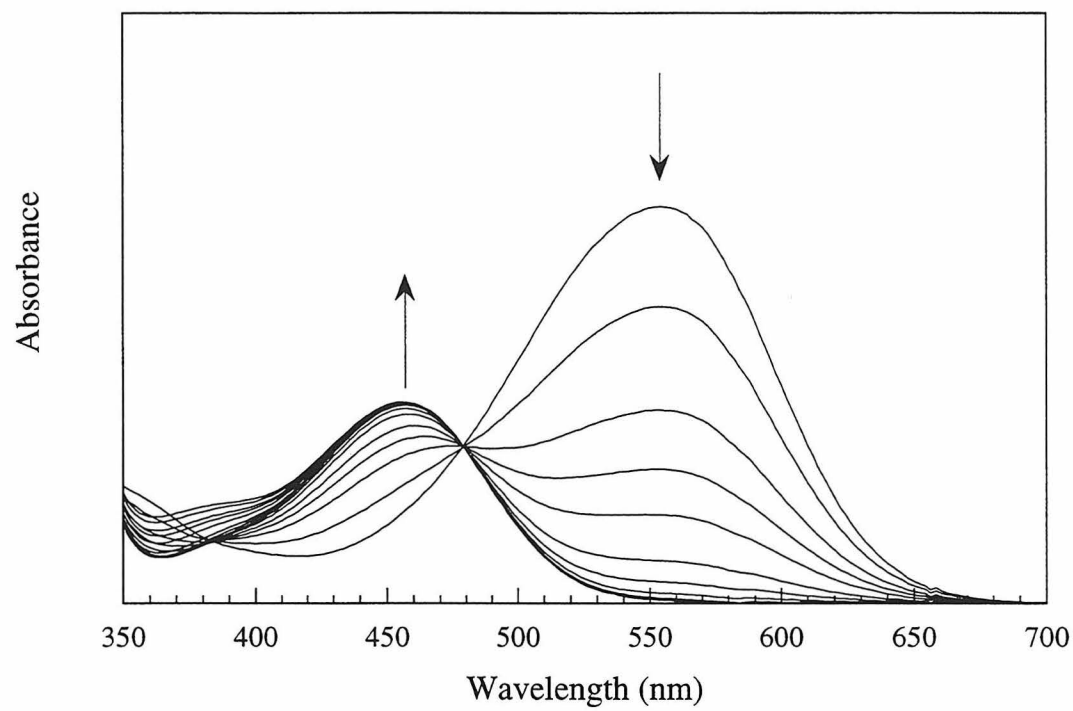
sulfur atom of the bdt ligand. Of course, d^8 complexes also can undergo oxidative addition of alkyl halides;⁷²⁻⁷⁴ thus, a platinum(IV) species is an equally plausible product. The ^1H NMR spectrum of $\text{Pt}(\text{bpy})(\text{bdt})$ in d_6 -dmso shows is composed of six multiplets between 6.6 and 9.2 ppm corresponding to the aryl protons of the C_{2v} symmetric complex. Addition of CH_3I causes these resonances to gradually lose intensity with the concomitant emergence of a new pattern of 12 multiplets with equal integration between 7 and 9.2 ppm, as expected for a C_s symmetric product. This result is most consistent with an initial reaction involving thiolate methylation:



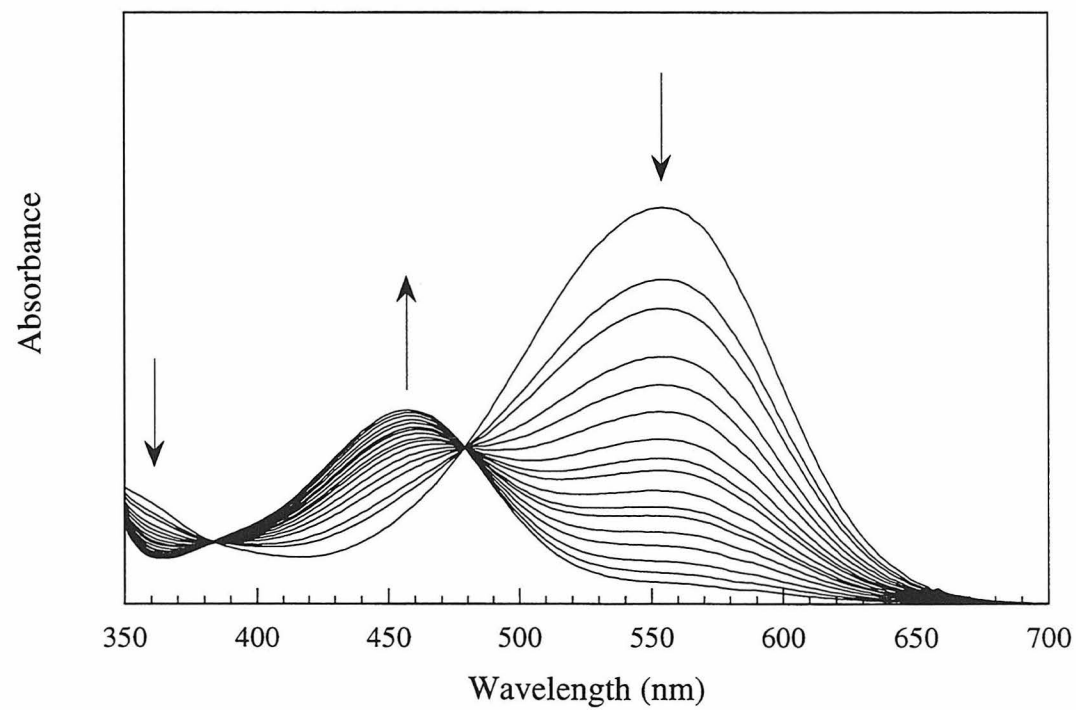
The longer timescale process observed in the absorption spectra could involve methylation of the other thiolate sulfur. The $\sim 4000\text{ cm}^{-1}$ per methyl group shift of the lowest absorption band to higher energy is consistent with the proposed products. Methylation of the sulfur ligand is expected to destabilize the LLCT state. Most likely, the blue-shifted bands (458 and 386 nm) in the spectra of the products have more MLCT character than the metal-mixed LLCT transition of the starting material. Overall, this type of reactivity is consistent with the expected nucleophilicity of the sulfur atoms of the bdt ligand. In analogy to other studies,⁶⁷⁻⁷⁰ the reaction is expected to involve nucleophilic attack by the sulfur on the CH_3I . The exact details are an intriguing question and warrant further investigation. In the case of square planar $\text{Ni}(\text{II})$ complexes, a pre-equilibrium step is proposed involving association of the metal complex and the alkyl halide; the metal serves to polarize the R-X bond, thereby promoting alkylation at the sulfur.⁶⁷⁻⁶⁹ Additionally, studies of ruthenium(II) thiolates suggest that π -backbonding enhances the thiolate nucleophilicity.⁷⁰

Figure 6.5 Absorption spectra recorded during reaction of Pt(bpy)(bdt) with CH₃I in dmf: (a) 0-135 minutes; (b) 0-29 minutes. Early in the course of the reaction (b), the absorbances at 384 and 478 nm do not change (pseudo-isosbestic points). However, at longer times (a) the absorbances change at these wavelengths, suggesting the occurrence of more than one chemical process.

(a)



(b)



Vogler has noted that Pt(bpy)(tdt) is photochemically unstable in chloroform solution (577 nm). We observe similar reactivity for the bdt complex; the LLCT absorption band loses intensity and shoulder emerges near 390 nm. We note, however, that the photoinduced reactions with CHCl_3 and CH_2Cl_2 appear to occur more slowly than the reaction with oxygen in air-saturated solutions (*vide infra*). Vogler has proposed that in the presence of chloroform, the tdt complex is oxidized resulting in the formation of Cl^- and $\cdot\text{CHCl}_2$ radical with subsequent steps leading to the observed degradation. Our results indicate that sulfur is a likely site for attack.⁷⁵

F. Photooxidation

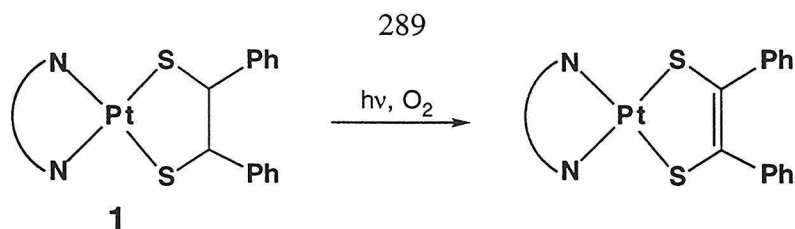
1. Background

In a series of papers, Srivastava and co-workers¹⁹⁻²² have demonstrated that *dozens* of platinum(II) and palladium(II) diimine complexes sensitize the formation of excited-state $^1\text{O}_2$ from ground-state triplet molecular oxygen ($^3\text{O}_2$). These studies are largely motivated by the possible role of these complexes as antitumor agents that exploit the cytotoxicity of both the metal complex and photogenerated $^1\text{O}_2$. Since the most effective sensitizers show a low-energy metal-mixed LLCT band, Srivastava and co-workers have focused on complexes with chelating dianionic ligands, such as catecholate and toluenedithiolate. In the course of these investigations,²³⁻²⁸ it was established that Pt(II) and Pd(II) diimine complexes with thiolate ligands undergo photoinduced decomposition in the presence of oxygen. The reaction is readily monitored by the disappearance of the LLCT band in the absorption spectrum as the red or violet solution becomes yellow. Steady-state quenching and trapping studies provide strong evidence for the involvement of $^1\text{O}_2$ in this process; however, the products of this reaction have not been identified.

Very recently, Schanze and co-workers²⁹ have reported on the photooxidation chemistry of two platinum(II) diimine dithiolate complexes in acetonitrile:

Pt(tbubpy)(dpdt) (**1**) and Pt(tbubpy)(edt) (**2**) (tbubpy=4,4'-di-*tert*-butyl-2,2'-bipyridine; dpdt=*meso*-1,2-diphenyl-1,2-ethanedithiolate; edt=1,2-ethanedithiolate). The reactivity of **2** is similar to that of compounds studied by Srivastava and co-workers; irradiation of an air-saturated solution resulted in a gradual bleaching of the LLCT band (466 nm) and other visible charge-transfer features. In contrast, irradiation of an air-saturated solution of **1** caused bleaching of the LLCT band (466 nm) accompanied by the emergence of a new band at *longer* wavelength (582 nm). This unusual behavior appears to characterize a novel type of photoreactivity for platinum(II) diimine dithiolate complexes. The authors have provided a painstaking analysis that largely confirms the conclusions of Srivastava, namely that these reactions involve singlet oxygen. In addition to quenching studies, a telling result was obtained by recording transient visible absorption spectra after initiating the reaction with a 10 ns laser pulse. For both **1** and **2**, the excited state is rapidly quenched by oxygen resulting in a fast decay (<15 ns) of the excited-state transient absorption spectrum. During the ensuing 500 ns, *no transient species was detected* in the visible absorption spectrum. However, at longer times (1-50 μ s), spectral changes associated with formation of the product were observed corresponding to an observed rate constant (k_{obs}) of $9.3 \times 10^4 \text{ s}^{-1}$. These results suggest that the reaction does not involve excited-state electron transfer to produce superoxide (O_2^-). In fact, they are entirely consistent with sensitization of $^1\text{O}_2$ which does not strongly absorb in the visible region and has a lifetime of $\sim 55 \mu\text{s}$ in acetonitrile.⁷⁶ The longer timescale kinetics are consistent with a bimolecular reaction involving $^1\text{O}_2$ and the ground-state platinum complex.

The products of the reactions of **1** and **2** with oxygen have not been fully characterized. However, for the novel reaction involving **1**, the UV-visible absorption and ^1H NMR spectra, as well as the mass spectrum, are consistent with loss of two H atoms to form the dithiolene adduct:



The products of the reaction involving **2** were insufficiently soluble for NMR studies, however, the mass spectrum suggests that the reaction involves addition of oxygen to the metal complex. In analogy to studies of the oxidation of nickel and palladium dithiolates,⁷⁷⁻⁷⁹ Schanze and co-workers propose several possible products, namely the corresponding sulfinato, disulfenato and disulfonato analogues of **2** (*i.e.*, the sulfone, disulfoxide and disulfone).²⁹

2. Photooxidation of *Pt(bpy)(bdt)*

Violet-colored air-saturated solutions of *Pt(bpy)(bdt)* gradually turn yellow in the presence of visible light. Both oxygen and light are necessary for this transformation, and the reaction ceases when either of these reagents is removed. As evidence of its thermal stability to oxygen, the crystal of *Pt(bpy)(bdt)* used for structural studies was grown by slow cooling of a boiling dmf solution protected from light. In short, the photoreaction appears qualitatively similar to the reactions studied by Srivastava²³⁻²⁸ and the decomposition of **2** observed by Schanze and co-workers.²⁹ UV-visible absorption spectra recorded while irradiating ($\lambda_{\text{ex}} > 450$ nm) an acetonitrile solution of *Pt(bpy)(bdt)* show that the LLCT band at 542 nm decays as a new band emerges at ~464 nm (Figure 6.6a). Early in the course of the reaction, the absorbances at 326 and 471 nm change (pseudo-isosbestic points); however, at longer times spectral changes occur at these wavelengths. This behavior suggests the occurrence of more than one chemical process, and kinetic analyses indicate that these data are well modeled as an $A \rightarrow B \rightarrow C$ type process. In principle, global fitting of these spectra can be used to extract the absorption spectra for each of these products. Plots of the logarithm of the absorbance at wavelengths where the products do not absorb ($\lambda > 550$ nm) are linear, as expected for a

pseudo first-order reaction. We observe similar behavior in dmf and dmso solutions, though the reaction is sluggish in dmso.⁸⁰

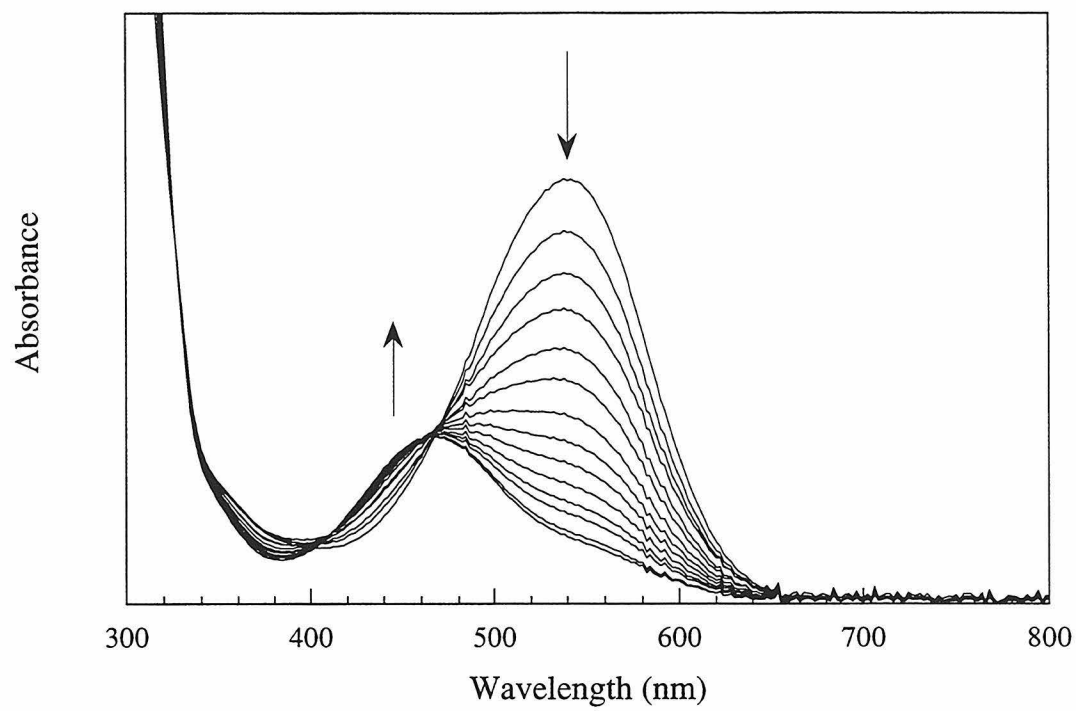
We have followed the course of the reaction by ^1H NMR in both d_6 -dmso and d_7 -dmf solutions. Irradiation ($\lambda > 400$ nm) of a dmso solution causes the intensity of the 6 resonances (6.6-9.2 ppm) in the spectrum of the starting material (A) to gradually decrease while the intensity of 12 new resonances with equal integration increases. The reaction in dmso is relatively sluggish, and after two days, only ~25% of the starting material had reacted.⁸⁰ In contrast, the photoreaction occurs more rapidly in dmf allowing for the observation of several products (Figure 6.7). During these studies we noted a remarkable acceleration in the reaction as the solvent absorbed moisture from the atmosphere. The initial product (B) is characterized by 12 resonances (7-9.8 ppm) which gain intensity at the expense of the $\text{Pt}(\text{bpy})(\text{bdt})$. Further irradiation yields a second product (C), characterized by 6 new resonances with equal integration (7.7-9.6 ppm). Eventually the starting material is entirely consumed, and C continues to increase in concentration at the expense of B. These data suggest an $\text{A} \rightarrow \text{B} \rightarrow \text{C}$ type process (Figure 6.7).

Further irradiation of the NMR sample leads to additional products D and E. The spectra of these products were not fully resolved because of overlap with the spectrum of C. However, it is clear that the spectrum of D is composed of at least 10 resonances with equal integration (7.7-9.9 ppm). Product E appears to form after some build-up of D; the spectrum of E is characterized by at least 5 resonances with equal integration (7.3-8.8 ppm). Unfortunately, shortly after B is entirely consumed, precipitation occurs preventing further monitoring of the reaction. At the point of precipitation, the NMR spectrum suggests that C is the major product in solution (60-80%), along with minor products, E and F.

In summary, we find that the ^1H NMR data are consistent with the overall sequential reaction: $\text{A} \rightarrow \text{B} \rightarrow \text{C} \rightarrow \text{D} \rightarrow \text{E}$. However, we emphasize that the last two steps

Figure 6.6 Absorption spectra recorded during the photooxidation of Pt(bpy)(bdt) in acetonitrile while irradiating with a tungsten lamp (150 W; $\lambda > 450$ nm), (a) 0-165 minutes and (b) 0-30 minutes. Early in the course of the reaction (b), the absorbances at 326 and 471 nm do not change (pseudo-isosbestic points). However, at longer times the absorbances change at these wavelengths (a), suggesting the occurrence of more than one chemical process. For $\lambda > 540$ nm, that is wavelengths where the products absorb only weakly, the natural logarithm of the absorbance is a linear function of time, as expected for pseudo-first-order kinetics. The plot of the logarithm of absorbance at $\lambda = 580$ nm is shown in the inset in (b).

(a)



(b)

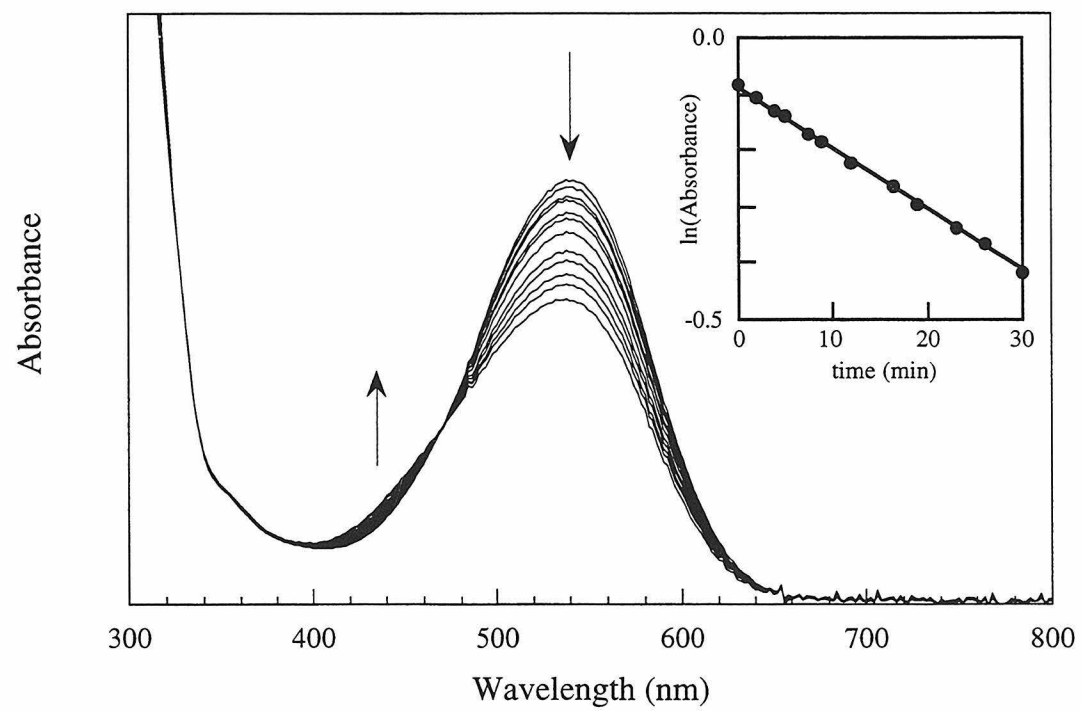
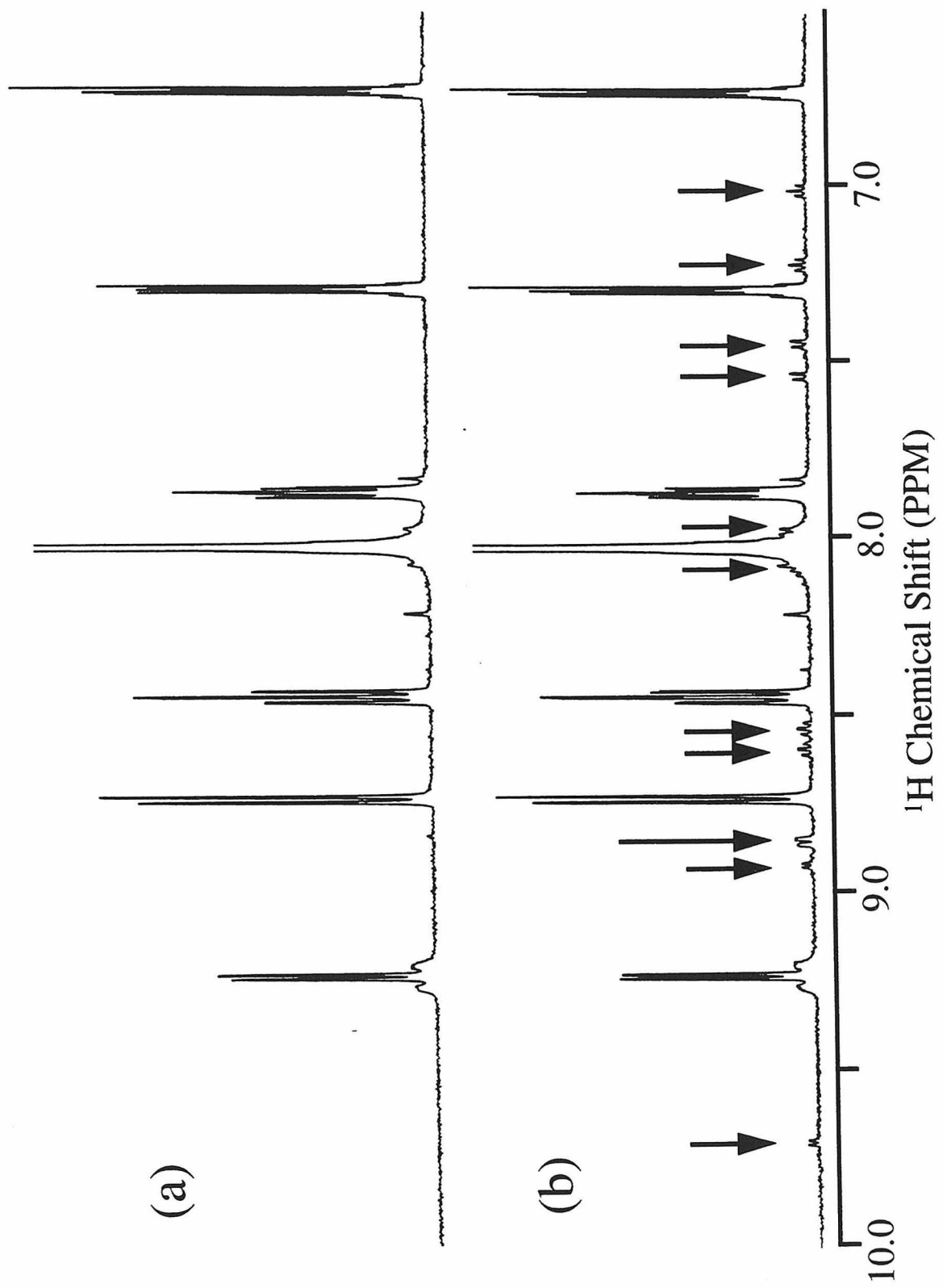
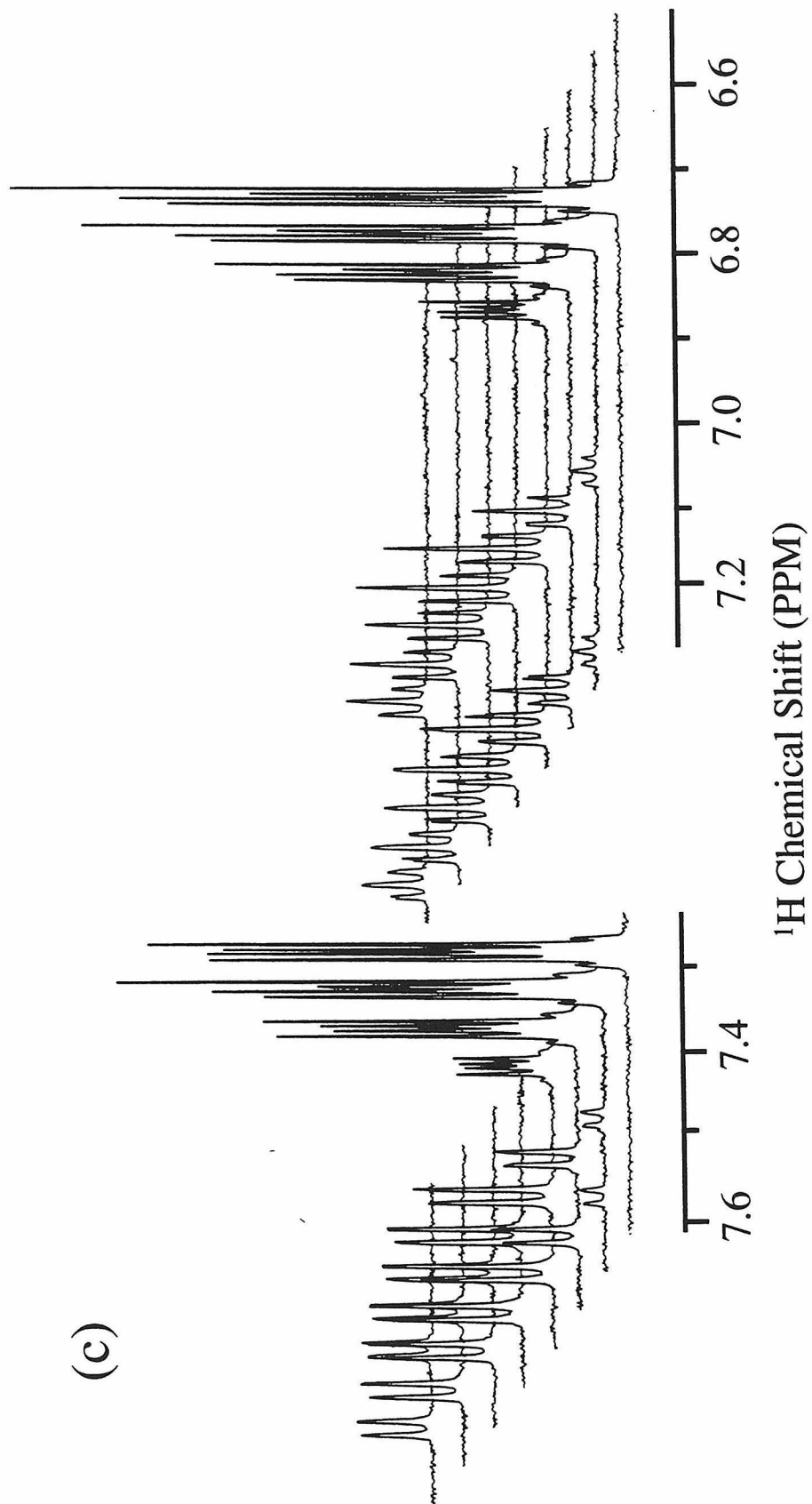


Figure 6.7 (a) ^1H NMR spectrum of $\text{Pt}(\text{bpy})(\text{bdt})$ in $\text{d}_7\text{-dmf}$. The effects of coupling to ^{195}Pt (34% natural abundance) are evident near 9.22 (bpy: 6,6'-H) and 6.72 (bdt: 3,6-H) ppm. Resonances at 7.83, 7.98, 8.01, 8.05, and 8.21 ppm also occur in the solvent blank. (b) ^1H NMR spectrum after eight minutes of irradiation ($\lambda > 450$ nm). The 12 resonances corresponding to the C_s symmetric $\text{Pt}(\text{bpy})(\text{bdtO}_2)$ product are marked with arrows. (c-d) Enlarged regions of ^1H NMR spectra recorded during the photooxidation reaction. In (c), over time the 2 resonances corresponding to $\text{Pt}(\text{bpy})(\text{bdt})$ gradually lose intensity, whereas 4 resonances corresponding to $\text{Pt}(\text{bpy})(\text{bdtO}_2)$ emerge and then begin to lose intensity. In (d), resonances due to $\text{Pt}(\text{bpy})(\text{bdt})$ (A), $\text{Pt}(\text{bpy})(\text{bdtO}_2)$ (B), $\text{Pt}(\text{bpy})(\text{bdtO}_4)$ (C), and the unidentified product, D, are observed. Bands corresponding to these products were identified by observing spectral changes during the reaction. Analysis of these spectra indicates that the products are formed in sequential steps: $\text{A} \rightarrow \text{B} \rightarrow \text{C} \rightarrow \text{D} \rightarrow \text{E}$. (Resonances corresponding E do not appear in (a-d).)





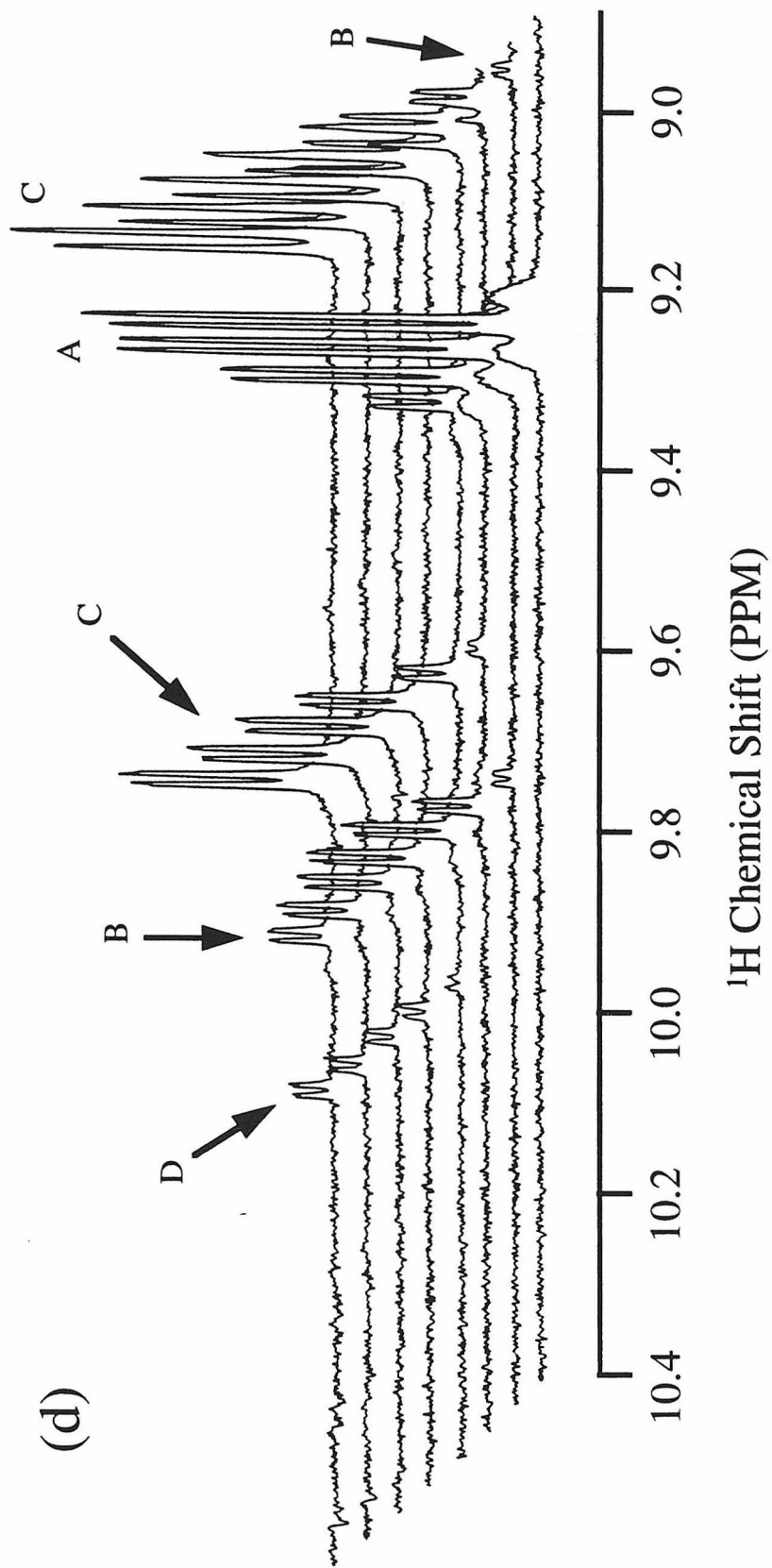
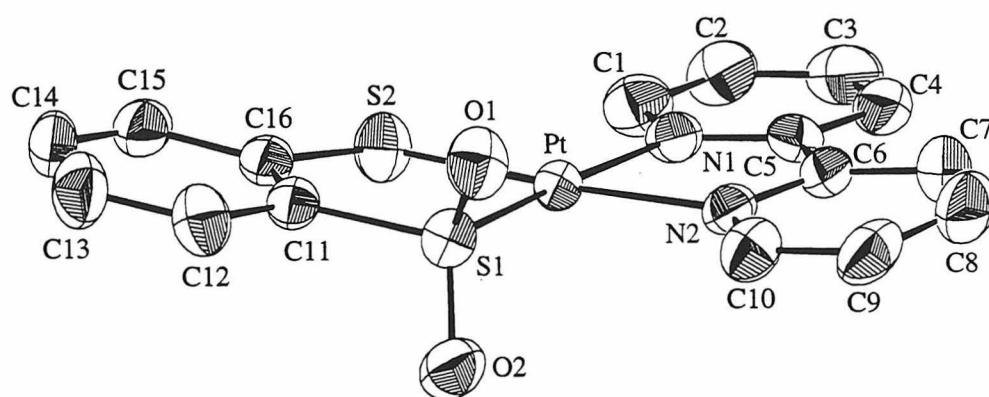
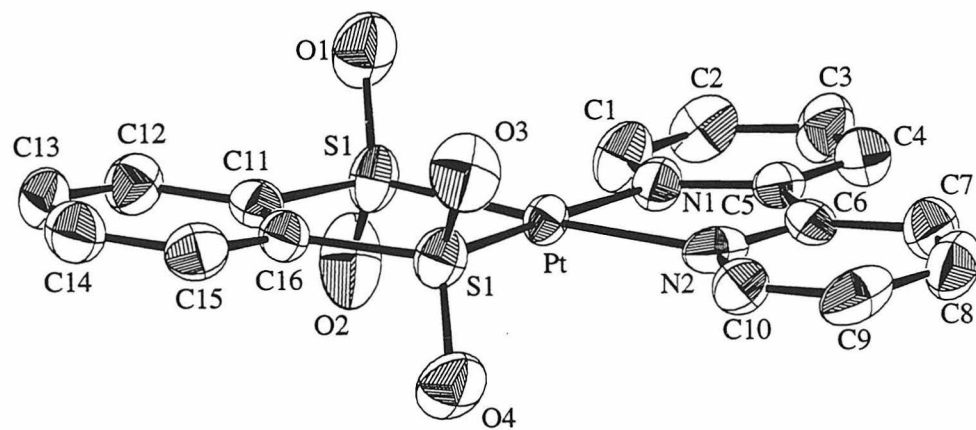


Figure 6.8 *ORTEP*II diagrams with 50% probability ellipsoids showing the geometry of the photooxidation products (a) Pt(bpy)(bdtO₂) and (b) Pt(bpy)(bdtO₄). The disordered atoms, O3 and O4, bound to S2 are not shown in (a). H atoms are omitted for clarity.

(a)



(b)



are difficult to characterize due to precipitation. Simultaneous monitoring of the UV-visible absorption spectrum of the NMR sample indicates that at the point of precipitation, the products (mainly C) are essentially non-absorbing between 400 and 700 nm. Thus, the UV-visible spectral changes are consistent with an $A \rightarrow B \rightarrow C$ type process. Moreover, the ^1H NMR spectra also indicate that the first product (B) has C_s symmetry whereas the second product (C) has the same symmetry as the starting $\text{Pt}(\text{bpy})(\text{bdt})$ complex, namely C_{2v} symmetry. Similarly, E and F could be C_s and C_{2v} symmetric products, respectively. These ^1H NMR spectra are in general agreement with oxidation to form the C_s symmetric sulfinato and C_{2v} symmetric disulfinate products.

3. Structures of the Photoproducts

Surprisingly, the fact that the photoproducts B and C are less soluble than the starting material has greatly aided in their characterization. For example, evaporation of a dmf solution of concentrated $\text{Pt}(\text{bpy})(\text{bdt})$ exposed to air and room-light ($\lambda > 400$ nm) yielded an orange-yellow residue and small yellow crystals containing C.⁸¹ A single crystal selected for X-ray diffraction studies was found to be composed of water of crystallization and the disulfinate oxidation product, $\text{Pt}(\text{bpy})(\text{bdtO}_4)$, in which each sulfur is bonded to two oxygen atoms (Figure 5.8b). The ^1H NMR spectrum of the bulk material in dmso shows 6 resonances with equal integration (7.6-9.4 ppm). The spectrum of B is evident as the minor product (~15%).

In a similar experiment, evaporation of an acetonitrile solution of $\text{Pt}(\text{bpy})(\text{bdt})$ exposed to air and room-light yielded yellow-orange crystals containing B. Presumably the lower solubility of the photoproducts in acetonitrile lead to some precipitation of B before further reaction to form $\text{Pt}(\text{bpy})(\text{bdtO}_4)$. A single crystal selected for X-ray analysis was found to be largely composed of the monosulfinate oxidation product, $\text{Pt}(\text{bpy})(\text{bdtO}_2)$, where two oxygen atoms have been added to one sulfur atom of the bdt ligand (Figure 6.8a). This C_s symmetric product is in agreement with the ^1H NMR and

visible absorption spectra.³⁵ The structure is disordered, and the oxygen atoms O1 and O2 that are bound to S1 have 90% site occupancy; atoms O3 and O4 that are bound to S2 have lower occupancy, but still greater than 10%. Since the UV-visible absorption and ¹H NMR spectra are consistent with a mixture of B and Pt(bpy)(bdtO₄), we have modeled the diffraction data as a mixture of both products.³⁵ From the oxygen site occupancies, we find 84% Pt(bpy)(bdtO₂) and 14% Pt(bpy)(bdtO₄).

The distances and angles for the carbon atom framework of both Pt(bpy)(bdtO₄) and Pt(bpy)(bdtO₂) are normal. The Pt-S(sulfinate) bonds are short (2.22 Å), indicating a strong Pt-S interaction. The approximately tetrahedral geometry of the sulfinate S atoms and the 1.45 Å S-O bond lengths are in excellent agreement with structures of other transition metal sulfinate complexes.^{77,79,82-86} In the case of Pt(bpy)(bdtO₂), the unreasonable S2-O distances (1.27(2), 1.61(2) Å) are an expected result of the disorder.

4. Kinetics Studies

We have monitored the initial photoreaction involving conversion of Pt(bpy)(bdt) to Pt(bpy)(bdtO₂) by observing changes in the UV-visible absorption spectrum during steady-state irradiation (λ_{ex} 514 nm). Values for k_{obs} were determined from the negative slopes of linear fits to plots of the logarithm of absorbance as a function of irradiation time; only data collected during the decomposition of the first 15% of the starting material were fitted. For a given sample, the slopes were essentially invariant for measurements at wavelengths longer than 540 nm - that is, in the region where the products do not absorb. Initially we encountered difficulties in obtaining reproducible data; however, once it was recognized that k_{obs} is extremely sensitive to water concentration, reproducible results were obtained using acetonitrile/water mixtures of known concentrations (Figure 6.9a).

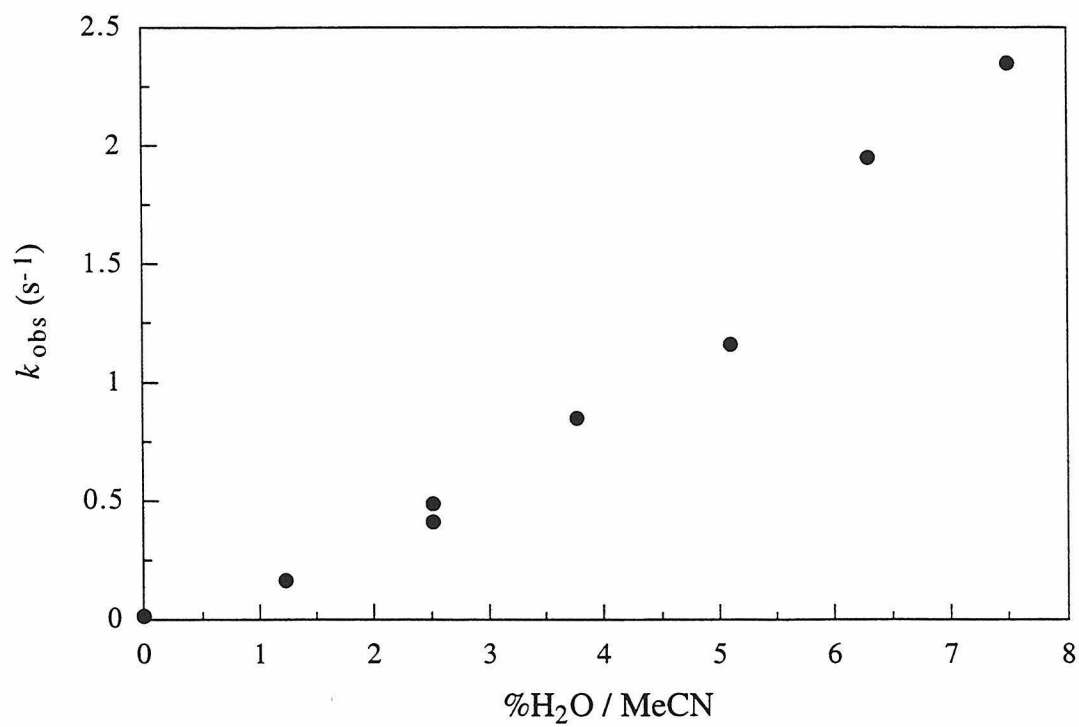
Under the conditions of our experiments, quenching to form the reactive oxygen species is very efficient since an O₂-saturated 2.5% H₂O/CH₃CN solution only reacted

25% more rapidly than an air-saturated solution. The strong water dependence is illustrated by the observation that k_{obs} for a 7.50% $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (0.13 mM $\text{Pt}(\text{bpy})(\text{bdt})$) solution is ~ 7 times greater than for a 1.23% $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ solution and 120 times greater than a $\sim 0.01\%$ $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ solution. Interestingly, the rate determined for the reaction in 2.5% $\text{D}_2\text{O}/\text{CH}_3\text{CN}$ was indistinguishable from that determined for the reaction in 2.5% $\text{H}_2\text{O}/\text{CH}_3\text{CN}$. On the other hand, the reaction was dramatically accelerated in a deuterated acetonitrile solution (2.5% H_2O / 2:1 $\text{CD}_3\text{CN}:\text{CH}_3\text{CN}$). This result is entirely consistent with the increased lifetime of singlet oxygen in deuterated solvents (τ : CH_3CN , 55 μs ; CD_3CN , 600 μs).^{87,88} Similarly, we observe a rate enhancement when Rose Bengal is added to the solution as a sensitizer.

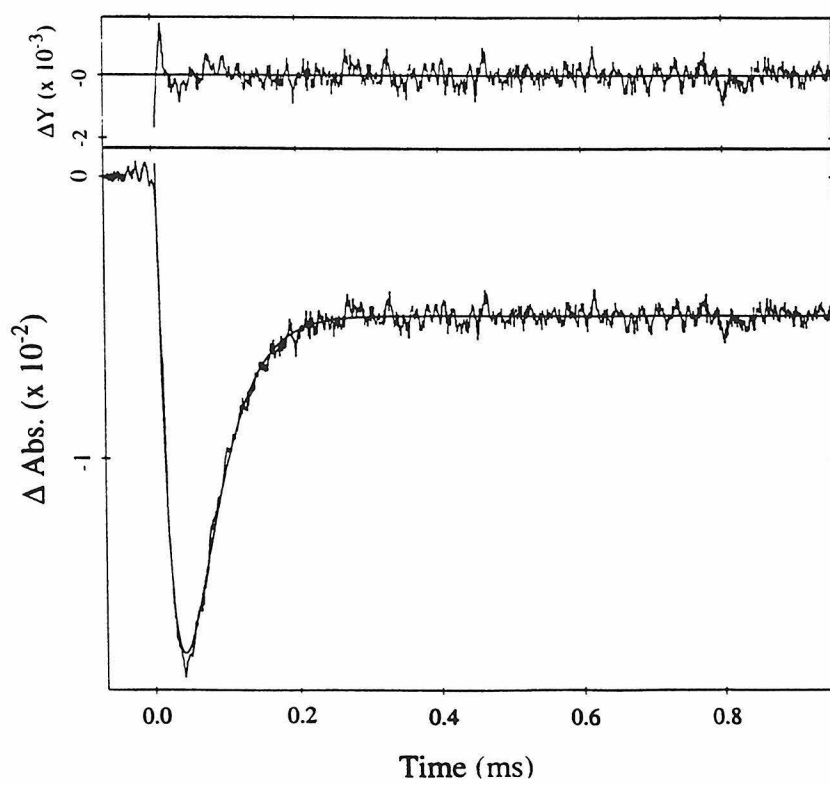
The most intriguing results were obtained by time-resolved absorption spectroscopy after initiation of the reaction with a 532 nm laser pulse. In degassed acetonitrile, the LLCT excited-state decays at the same rate as the emission; the lifetime is essentially unchanged in degassed 3.5% $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ solution. The transient absorption spectrum of the excited $\text{Pt}(\text{bpy})(\text{bdt})$ complex is shown in Figure 6.9b. In order to enhance signal-to-noise, we have recorded the transient absorption spectra of a series of air-saturated water(0-18%)/acetonitrile solutions. These results are summarized as follows. The excited-state is rapidly quenched (< 20 ns) in the presence of oxygen. *During the ensuing microsecond following excitation, no transient species are detected in the absorption spectrum.*⁸⁹ This result confirms that no reduced or oxidized platinum species is generated as a result of the quenching of excited-state by O_2 . Thus, $^1\text{O}_2$ appears to be the initial reactive oxygen species. Indeed, at longer times (1-250 μs), at least two processes are clearly observed. Biexponential fits suggests the rate constants have similar magnitudes, $\sim 2\text{-}5 \times 10^4 \text{ s}^{-1}$. Nevertheless, they are clearly distinguishable since the consistently faster process leads to a bleach at 550 nm, while the other leads to a relative increase; the result is a characteristic and reproducible “potential well” shaped signal (Figure 6.9). The resulting transient signal after 1 ms appears to persist (or at least

Figure 6.9 (a) Observed pseudo-first-order initial rate constants (k_{obs}) for the steady-state photooxidation of Pt(bpy)(bdt) in aqueous acetonitrile as a function of %water content (λ_{obs} 580 nm, 15% depletion; λ_{ex} 514 nm, 0.01 mW). (b) Transient absorption kinetics at 550 nm following laser flash excitation (λ_{ex} 532 nm, 10 ns, 1 mJ) of an air-saturated 0.1 mM Pt(bpy)(bdt) 10% H₂O / acetonitrile solution. The smooth line is the fit to the biexponential function: $C_0 + C_1 e^{-k_1 t} + C_2 e^{-k_2 t}$ (C_0 , -4.9×10^{-3} ; C_1 , 2.0×10^{-1} ; C_2 , -1.9×10^{-1} ; k_1 , $3.5 \times 10^4 \text{ s}^{-1}$; 2.8×10^4 k_2 , s^{-1}). (c) Transient absorption spectrum of excited Pt(bpy)(bdt) in degassed acetonitrile solution (λ_{ex} 532 nm, 10 ns, 1 mJ) data points at time=0 were extrapolated from fits to the single exponential excited-state decay at each wavelength. (d) Transient absorption spectrum of an air-saturated 0.1 mM Pt(bpy)(bdt) 10% H₂O / acetonitrile solution 1 ms after the excitation laser pulse (λ_{ex} 532 nm, 10 ns, 1 mJ). The solid curve corresponds to the absorbance difference spectrum for Pt(bpy)(bdt) and Pt(bpy)(bdt)⁺ obtained from chemical oxidation (Figure 6.4b).

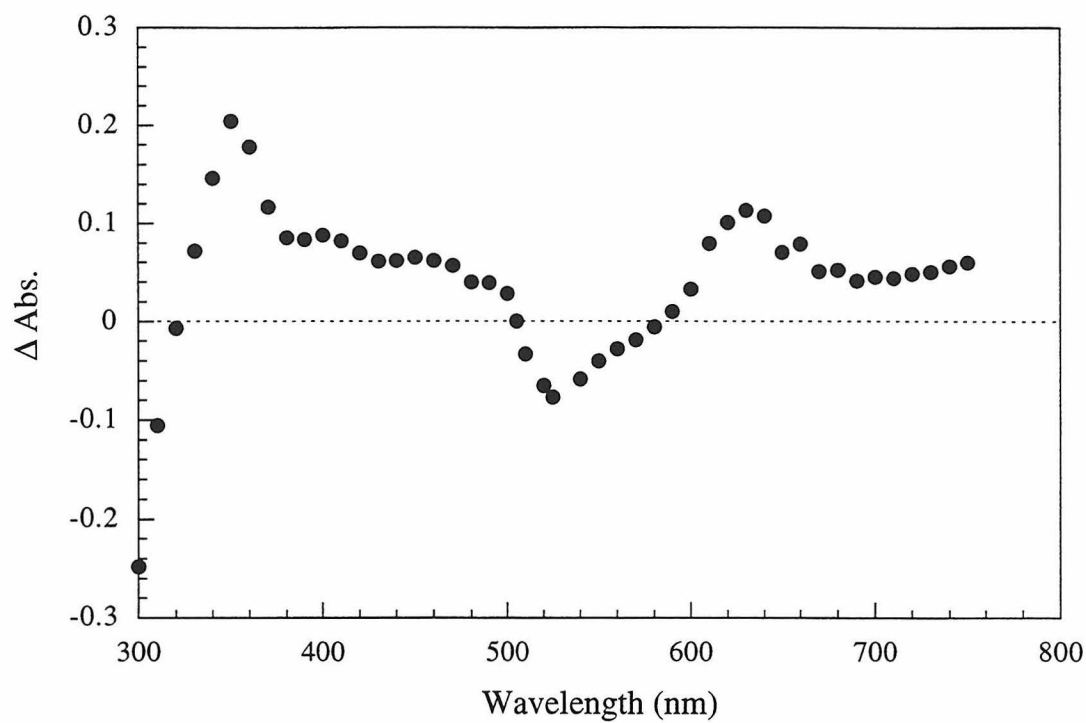
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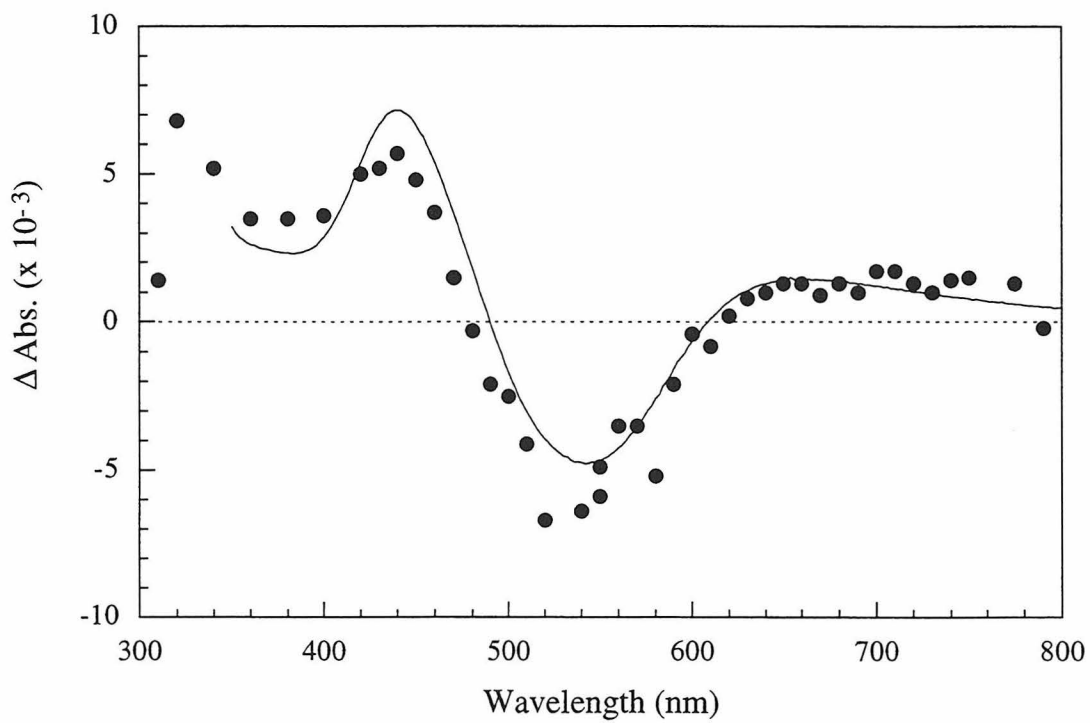
(b)



(c)



(d)



decay very slowly) for the next 75 ms; however, further measurements are necessary on these long timescales. The transient absorption spectrum at 1 ms is different from the excited-state spectrum; however, the agreement between this spectrum and the $\text{Pt}(\text{bpy})(\text{bdt})/\text{Pt}(\text{bpy})(\text{bdt})^+$ difference spectrum is remarkable (Figure 6.9d).

It also is striking that the rates of the two microsecond timescale processes are slightly faster than the excited-state decay of $^1\text{O}_2$ in acetonitrile ($1/\tau$, $2 \times 10^4 \text{ s}^{-1}$),⁸⁸ corresponding to a rate of singlet oxygen quenching by platinum of $\sim 10^8 \text{ M}^{-1}\text{s}^{-1}$. Interestingly, the transient signal at 560 nm for a 10% $\text{H}_2\text{O}/\text{CD}_3\text{CN}$ solution shows a single-exponential bleach that occurs approximately 2 times more slowly than the bleaching process observed for the undeuterated solvent mixture; the overall effect is an increased concentration of transient intermediate (in terms of change in optical density) at the one millisecond point. A similar single-exponential decay and enhanced yield is observed when Rose Bengal is added to the solution. In contrast, addition of azide ion (7 mM NaN_3), which is known to quench singlet oxygen, results in almost no transient signal. We also find that the rates of the microsecond timescale processes are only slightly affected by increasing water concentration between 3.3 and 14.3% $\text{H}_2\text{O}/\text{CH}_3\text{CN}$; however, the slower rate seems to sharply decrease in 17.9% $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (14.3% H_2O , 4×10^4 ; 17.9% H_2O , $6 \times 10^3 \text{ s}^{-1}$). On the other hand, the concentrations of intermediates at 40 μs and 1 ms increase, maximizing near 14% $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ for 1.1 mM $\text{Pt}(\text{bpy})(\text{bdt})$.

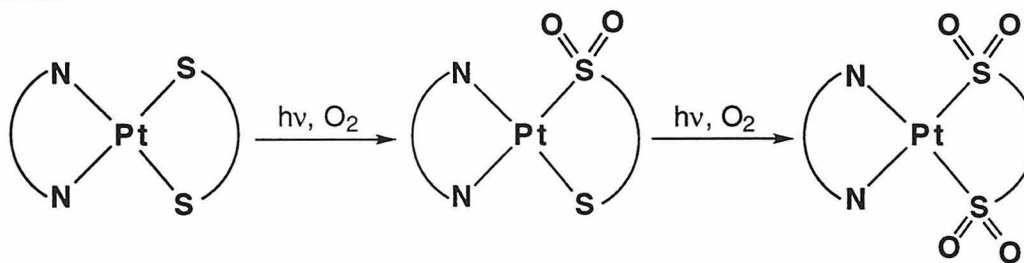
In summary, our kinetics measurements are entirely consistent with the involvement of singlet oxygen in the photooxidation reaction. The studies of Srivastava,²³⁻²⁸ and Schanze²⁹ also support this proposal. However, in contrast to Schanze's system, we find that there are two detectable processes on the 30 ms timescale; while these may be as simple as oxygen binding and dissociation, there are nevertheless two processes. Finally, the transient absorption spectrum obtained one millisecond after excitation *clearly does not correspond to either of the oxygenated products* that we have identified, namely $\text{Pt}(\text{bpy})(\text{bdtO}_2)$ and $\text{Pt}(\text{bpy})(\text{bdtO}_4)$. Admittedly, we have not yet

determined the absorption spectra for the photoproducts, nor is it certain that the transient absorption features correspond to a major product or productive intermediates.

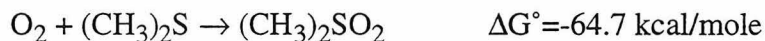
Nevertheless, the transient species clearly absorbs between 600 and 800 nm - that is, in a region where *neither* of the oxygenated products absorbs. In fact, the spectrum of this species is remarkably similar to that of the one-electron oxidized platinum complex. These results are consistent with the formation of $\text{Pt}(\text{bpy})(\text{bdt})^+$ and a corresponding reduced species such as O_2^- , or alternatively, the formation of a $\text{Pt}(\text{bpy})(\text{bdt})$ -oxygen complex with spectral features that are similar to $\text{Pt}(\text{bpy})(\text{bdt})^+$.

IV. Conclusion

$\text{Pt}(\text{bpy})(\text{bdt})$ reacts with oxygen in the presence of light to form sulfinated products:

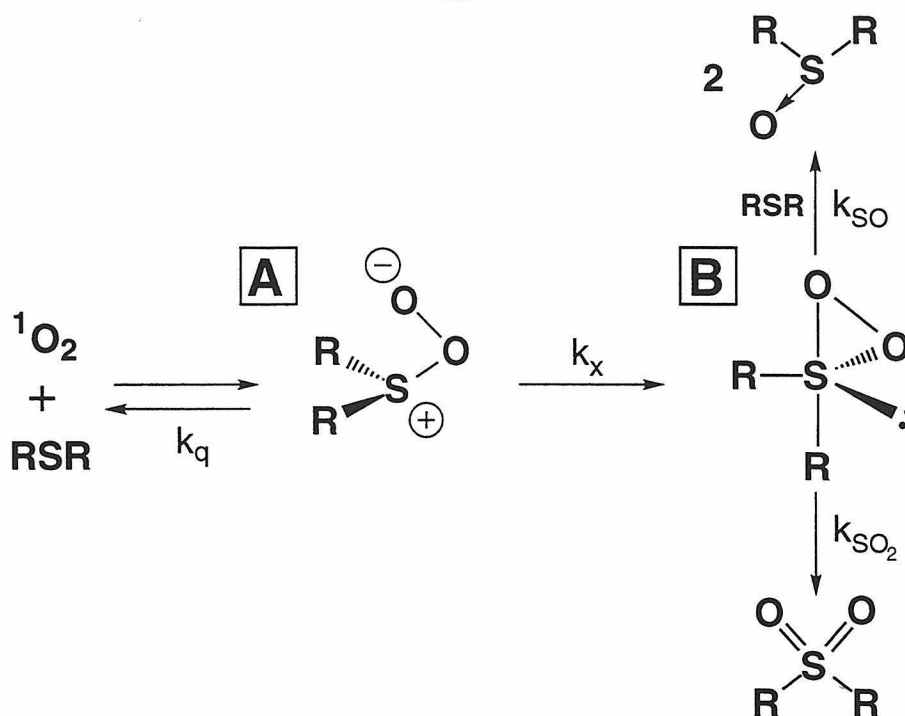


There is strong evidence for the involvement of singlet oxygen sensitized by the metal-mixed LLCT excited-state complex. We infer from thermodynamic data⁹⁰ that the conversion of $\text{Pt}(\text{bpy})(\text{bdt})$ to its sulfinated derivatives is an overall favorable reaction:



The necessity of $^1\text{O}_2$ to carry out the oxidation of the Pt complex may be related to the spin-barrier for the reaction with $^3\text{O}_2$.

There is a close analogy between the singlet-oxygen reactivity of $\text{Pt}(\text{bpy})(\text{bdt})$ and that of alkyl sulfides. Since the latter process has been extensively studied, it seems a logical starting point for a mechanistic discussion. The mechanism proposed by Foote and co-workers⁹¹ involves formation of two intermediates, **A** and **B**:



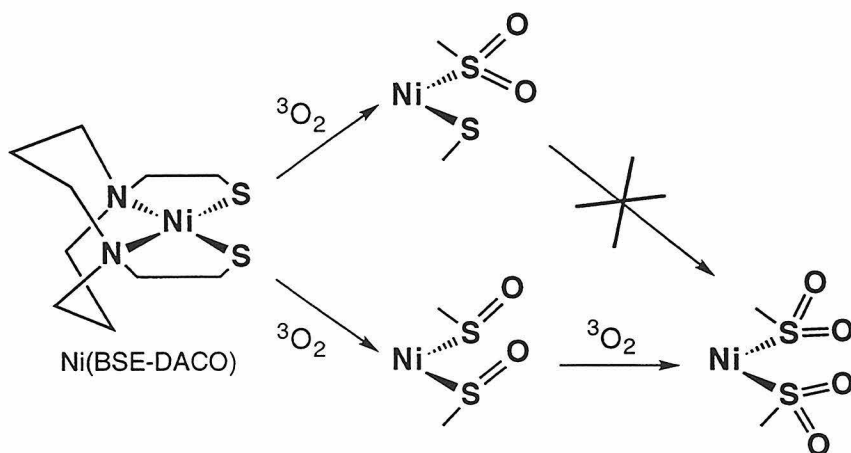
Though there is still considerable debate surrounding the details of this reaction,⁹²⁻⁹⁷ it is widely agreed that the zwitterionic persulfoxide, **A**, is initially formed by reaction of the sulfide with $^1\text{O}_2$. (There is some uncertainty as to whether the thiadioxirane, **B**, is formed in competition with **A** or subsequent to **A**.)⁹² In aprotic solvents, physical quenching dominates (>95%). However, in protic solvents (*e.g.*, methanol or aqueous acetonitrile)⁹⁸ the sulfide oxidation is efficient and no physical quenching is detected. In that case, the persulfoxide intermediate **A** is proposed to be stabilized by hydrogen bonding or solvent addition to form a sulfurane (*e.g.*, $\text{R}_2(\text{OO})\text{S}-\text{solvent}^+$), thereby allowing for rearrangement to **B** which collapses to form products.

It is striking that we also observe a dramatic acceleration in the rate of oxidation when water is added to an acetonitrile solution of $\text{Pt}(\text{bpy})(\text{bdt})$. Thus, we conclude that a reasonable intermediate for this reaction is persulfoxide-type intermediate proposed for the sulfide system. Indeed, the transient absorption kinetics are consistent with an oxygen binding step. It also is intriguing that the long-lived transient 1 ms after laser excitation is remarkably similar to the spectrum of the oxidized Pt complex (Figure 6.9d).

It is not unreasonable that this spectrum arises from the transient zwitterionic persulfoxide intermediate which might be expected to have an absorption profile very much like one-electron oxidized Pt(bpy)(bdt). This suggestion is tantalizing since the intermediates in the organosulfide reactions have *never* been directly observed.

A reasonable alternative is that the long-lived transient is, in fact, Pt(bpy)(bdt)⁺. In that case, a likely candidate for the reduced species is O₂⁻ which slowly oxidizes the complex. This situation is equally fascinating since it implies that the excited complex undergoes energy transfer with ³O₂ to generate ¹O₂ — *with which it later reacts to form superoxide*. The surprising result is that O₂⁻ is not generated in the initial excited-state quenching reaction, although there is clearly considerable driving force for this process: Pt(bpy)(bdt)* + ³O₂ → Pt(bpy)(bdt) + ¹O₂, ΔG° ~ -1.2 V. One explanation is that the excited-state ET reaction is kinetically disfavored because it is highly inverted, whereas the subsequent conversion of ¹O₂ to superoxide has a much lower driving force (ΔG° ~ -0.5 V).⁹⁹

The reactivity of Pt(bpy)(bdt) is apparently not identical to that of organic sulfides. In particular, we have not observed formation of stable sulfenated products (*e.g.*, Pt(bpy)(bdtO)). In contrast, Darensbourg and co-workers have demonstrated that Ni dithiolate complexes react thermally with ³O₂ to form sulfenates and sulfinates:



Moreover, these studies have established that the once the sulfinato is formed, it is inactive toward addition of second molecule of oxygen. A dual-pathway mechanism is proposed involving a sulfenato intermediate. Our results agree, in that the Pt(bpy)(bdtO₂) product also seems stable in the presence of ground-state oxygen. However, this product is further activated by singlet oxygen (or another activated oxygen species), and we find no evidence of a sulfenato intermediate. It is hardly surprising that ³O₂ and ¹O₂ would lead to different reactivity. Recently, Darensbourg have reported preliminary data suggesting that Pd(BSE-DACO), in the presence of UV light and air, is converted to the monosulfinate (27-37%) and disulfinate (3%) products; however, few details have been given, and the photophysical properties of the Pd complex are not known.

We conclude by remarking that the reactions of sulfur compounds with oxygen are notoriously complex because the number of oxidation states of sulfur allows for a variety of stable intermediates and products.^{97,100,101} It is not known if Pt(bpy)(bdt) photooxidation involves multiple mechanisms depending on the reaction conditions. However, it is clear that at least one reaction pathway is strongly favored in aqueous acetonitrile. Because the bdt ligand is involved in the intense low-energy LLCT band, reactions involving the sulfur atoms lead to large changes in the visible region of the absorption spectrum. Thus, we have the rare opportunity to directly observe intermediates in a sulfur oxidation reaction using time-resolved spectroscopy.

V. References and Notes

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