3230 *Inorg. Chem.* **1992**, *31*, 3230–3235

Excited-State Properties of Platinum(II) Complexes Containing Biphenyl as a Ligand: Complexes of the Type [(bph)PtL$_2$], Where L = Monodentate or Saturated Bidentate Ligands

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Received October 23, 1991

The preparation, physical properties, and photophysical properties of [Pt(bph)($C_2H_5)_2$S]$_2$, [Pt(bph)($CH_3CN)_2$], [Pt(bph)(en)], and [Pt(bph)(py)$_2$], where bph^{2-} is the dianion of biphenyl, en is ethylenediamine, and py is pyridine, are described. The complexes display d$\pi \rightarrow \pi^*$ transitions in the 300–400-nm region and intraligand $\pi \rightarrow \pi^*$ transitions at higher energy. Only one redox process, an irreversible oxidation, is observed in the +2 to −2 V region. The $E_{1/2}$ values range from 0.67 to 1.35 V vs SSCE. Highly structured emission is observed and attributed to a ^{3}LC → ^{1}GS process. Spectral curve fitting using a four-mode fit gives $E_{00} \simeq$ 20 670 cm^{-1} and vibrational frequencies of 1550, 1150, 715, and 375 cm^{-1} that are nearly independent of the specific complex. Temperature-dependent lifetime data reveal the presence of an energy level above the ^{3}LC state with an activation energy of 1220 cm^{-1} for [Pt(bph)($CH_3CN)_2$], 2280 cm^{-1} for [Pt(bph)(py)$_2$], and 2490 cm^{-1} for [Pt(bph)(en)]. The energy gap of ~2.6 eV gives rise to high oxidative quenching power (−1.14 to −1.71 V) demonstrated by electron-transfer quenching with methyl viologen and *o*-nitrobenzene.

Introduction

The search for inorganic materials that would behave as energy- or electron-transfer photocatalysts in solution has primarily involved investigating the photochemical and photophysical properties of ruthenium(II), osmium(II), and rhenium(I) complexes.[1] Platinum(II) complexes have received less attention, but in the few cases published, platinum(II) complexes have been shown to have promising properties.[2-12] A number of these complexes luminesced strongly in solution, some underwent excited-state electron-transfer quenching, and some displayed photoassisted oxidative addition reactions.

These platinum(II) complexes can be divided into four types on the basis of their emitting states. Those classified as intraligand (IL) $\pi \rightarrow \pi^*$ emitters were Pt(II) complexes of 8-quinolinol chelates,[2] a [Pt(5,5′-dimethyl-2,2′-bipyridine)(CN)$_2$] adduct,[3] and a [Pt(2,2′-bipyridine)($NH_3)_2$]$^{2+}$–dibenzo[30]crown-10 adduct.[4] Those classified as interligand (LLCT) $\pi \rightarrow \pi^*$ emitters were Pt(II)dithiolate–diimine complexes.[5] The d$\pi \rightarrow \pi^*$ (MLCT) emitters were [Pt(diimine)(biphenyl)] complexes[6] and Pt(II) complexes containing 2-phenylpyridine and 2-(2-thionyl)pyridine ligands.[7,8] The final classification consists of complexes that emit from metal–metal excited states. Complexes demonstrating this property were [Pt$_2$(P$_2$O$_5$H$_2)_4$]$^{4-}$,[9] [Pt(CN)$_4$]$_n$$^{2-}$,[10] Pt$_2$[bis(diphenylphosphine)methane]$_2$(CN)$_4$],[11] and an excimer based on [Pt(4,7-diphenyl-1,10-phenanthroline)(CN)$_2$].[12]

In this report, we examine the physical and photophysical properties of a new series of Pt(II) complexes containing the biphenyl dianion as a ligand, which was expected to result in high-energy emission, provided emission occurred from the π^* energy level of the ligand. To ensure this, two synthetic strategies were used: (1) The bph ligand was coordinated in a bidentate fashion through the carbon atoms located in the 2,2′ positions of biphenyl; (2) the other ligand(s) chosen either had higher π^* energy levels than bph (pyridine, acetonitrile, diethyl sulfide) or were saturated alkylamines (ethylenediamine). We reported our initial success following this line of attack earlier.[13]

Experimental Section

Materials. Acetonitrile and methylene chloride were spectrophotometric grade and were dried over 4-Å molecular sieves before use in electrochemistry experiments. Tetrabutylammonium hexafluorophosphate (TBAH) was purchased as electrometric grade from Southwestern Analytical and stored in a vacuum oven before use. *n*-Butyllithium in hexane was provided by Lithco, Inc., a division of FMC. Reactions involving lithium alkyl reagents were carried out under a nitrogen atmosphere and handled by way of syringe techniques. Potassium tetrachloroplatinate was obtained on loan from Johnson-Matthey, Inc. All other reagents were purchased as reagent grade and were used without further purification.

Preparation of Compounds. The following compounds were prepared according to literature procedures: 2,2′-dibromobiphenyl (mp 77–78 °C (lit. 78–79 °C)),[14] 2,2′-dilithiobiphenyl,[15] [PtCl$_2$(($C_2H_5)_2$S)$_2$],[16] and [Pt(bph)($C_2H_5)_2$S]$_2$.[6a] The elemental analysis results for [Pt(bph)($C_2H_5)_2$S]$_2$ were as follows: Anal. Calcd for $Pt_2C_{32}H_{36}S_2$: C, 43.93; H, 4.15; S, 7.33. Found: C, 43.88; H, 4.17; S, 7.27.

[Pt(bph)(ethylenediamine)]. A 25-mL round-bottom flask was charged with 22 mg (2.55 × 10^{-5} mol) of [Pt(bph)($C_2H_5)_2$S]$_2$ and 0.020 mL of

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Table I. Visible/UV Spectral and Redox Properties

complex	λ^a		$E_{1/2}{}^b$	
	$d\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$[Pt(bph)L_2]^{+/0}$	$[Pt(bph)L_2]^{+/0*}$
$[Pt(bph)C_2H_5)_2S]_2$[c,d]	340 (2.3×10^4)	266 (3.7×10^4)	1.35 (irr)	−1.14
	310 (2.4×10^4)	252 (3.8×10^4)		
		235 (4.6×10^4)		
$[Pt(bph)(py)_2]$[d]	375 sh	275 (3.3×10^4)	0.81 (irr)	−1.85
	332 (4.0×10^3)	236 (1.1×10^4)		
	303 (3.8×10^3)			
$[Pt(bph)(CH_3CN)_2]$[e]	380, 357 sh	261 (1.4×10^4)	0.85 (irr)	−1.67
	326 (1.6×10^4)	258 (4.8×10^4)		
	302 (1.3×10^4)			
$[Pt(bph)(en)]$[d]	380, 357 sh	258 (4.8×10^4)	0.67 (irr)	−1.71
	333 (6.0×10^3)	233 (1.7×10^4)		
	305 (4.3×10^3)			

[a] $T = 23 \pm 1$ °C; λ in nm, error = ±1 nm; ε in M^{-1} cm^{-1}, error = ±0.1. [b] $T = 23 \pm 1$ °C; $E_{1/2}$ in V vs SSCE, error = ±0.02 V; 0.1 M TBAH; irr = irreversible. [c] Reference 6a. [d] In methylene chloride. [e] In acetonitrile.

diethyl sulfide dissolved in 15 mL of methylene chloride. To this stirred platinum solution was added dropwise 100 mg (1.50×10^{-3} mol) of ethylenediamine in 5 mL of methylene chloride. Immediately, the color changed from a light yellow to a deep yellow. Approximately 5 min later, a yellow-green precipitate began to form. The suspension was protected from light and was stirred for 30 min under nitrogen. A yellow-green luminescence was observed in the solid state. The precipitate was collected and washed with diethyl ether. Yield = 8 mg (50.6%). Anal. Calcd: C, 41.28; H, 3.96; N, 6.88. Found: C, 41.11; H, 4.00; N, 6.83.

$[Pt(bph)(pyridine)_2]$. A 50-mL round-bottom flask was charged with 19 mg (2.12×10^{-5} mol) of $[Pt(bph)(C_2H_5)_2S]_2$ and 0.030 mL of diethyl sulfide dissolved in 15 mL of methylene chloride. A solution of 0.80 mL (9.90×10^{-3} mol, $d = 0.978$ g/mL) of pyridine in 7 mL of methylene chloride was added dropwise to the stirred platinum solution. A yellow precipitate began to form midway through the addition. The suspension was protected from light and allowed to stir for 30 min. The precipitate was collected by vacuum filtration and washed with copious amounts of diethyl ether and hexane to remove the unreacted pyridine. A yellow-green luminescence was noted in the solid state. The product was then dried in a vacuum oven overnight. No further purification was required. Yield = 16 mg (74.3%). Anal. Calcd: C, 52.27; H, 3.59; N, 5.54; S, 0.00. Found: C, 52.00; H, 3.65; N, 5.46; S, 0.00.

$[Pt(bph)(CH_3CN)_2]$. A 50-mL round-bottom flask was charged with 10 mg (1.14×10^{-5} mol) of $[Pt(bph)(C_2H_5)_2S]_2$ and 20 mL of acetonitrile. This mixture was sonicated until a clear yellow solution was obtained. The solvent was removed by rotary evaporation, and a yellow solid was obtained. A yellow-green luminescence was observed in the solid state. No further purification was performed. Yield = 9 mg (90%). Anal. Calcd: C, 44.76; H, 3.29; N, 6.52; S, 0.00. Found: C, 44.95; H, 3.42; N, 6.17; S, trace.

Measurements. Visible/UV spectra were obtained with a Perkin-Elmer Model 3840 diode array spectrophotometer. Corrected emission spectra were recorded with a Spex Fluorolog Model 212 spectrofluorometer. Cyclic voltammograms were obtained using a three-electrode system consisting of a Pt-disk working electrode, a Pt-mesh counter electrode, and a saturated sodium chloride calomel electrode (SSCE). The electrochemical measurements were made with a PAR 174 polarographic analyzer or a PAR 173 potentiostat in conjunction with a PAR 175 programmer and recorded with a YEW Model 3022 A4 X-Y recorder.

Excited-state lifetimes were acquired using a Photochemical Research Associates (PRA) Model LN1000 pulsed N_2 laser and a PRA LN102 dye laser. The measurements were carried out with a LeCroy transient digitizer system employing either a 6880A or a TR 8828C transient recorder. The LeCroy 6010 controller was interfaced to an IBM PS/2 Model 60 microcomputer via a National Instruments GPIB IEEE-488 bus and controlled by Catalyst software supplied by LeCroy. Computations of time-dependent emission decays were performed by an in-house program, LIFETIME written by Randy J. Shaver, utilizing an algorithm designed to fit the data to a single-exponential decay. Temperature-dependent excited-state lifetime measurements were obtained by utilizing a Cryo Industries Model EVT cryostat controlled by a Lakeshore 805 temperature controller.

A Photon Technology, Inc., apparatus consisting of a PTI LPS 200X 74-W photolysis system, an Oriel Model 77250 monochromator, and a cell holder mounted on an optical rail was used for photolysis investigations. The cells were equilibrated at a temperature of 25 ± 1 °C in a Haake FK2 constant-temperature bath. The light intensity was determined at 355 nm using ferric oxalate[17] as the actinometer.

A neodymium–YAG laser system located at the University of North Carolina at Chapel Hill was used for laser flash photolysis measurements.

Computer fits of temperature-dependent lifetime data were obtained with an IBM PS/2 Model 60 microcomputer utilizing either an algorithm based on a nonlinear-least-squares analysis or an algorithm based on procedures outlined by Wentworth[18] which allows for variance in both plotted variables. The low-temperature emission spectral fits were performed with a simple algorithm based on a multimode vibrational analysis[19] and modified by Dr. Cliff Carlin of our department for anharmonicity of the vibrational modes.

Elemental analyses were carried out by Atlantic Microlabs, Inc., Norcross, GA.

Results

Preparation of Complexes. $[Pt(bph)(C_2H_5)_2S]_2$ served as the starting material in the synthesis of $[Pt(bph)L_2]$ and $[Pt(bph)(L\text{-}L)]$ complexes, where L = acetonitrile (CH_3CN) and pyridine (py) and L-L = ethylenediamine (en). The synthesis involved addition of $(C_2H_5)_2S$ to the starting material in methylene chloride followed by addition of the desired ligand to yield the reported complexes with one exception. Thermal displacement of $(C_2H_5)_2S$ by CH_3CN was effected in acetonitrile without added $(C_2H_5)_2S$. Presumably, added $(C_2H_5)_2S$ facilitates formation of a monomer/dimer equilibrium, $[Pt(bph)(C_2H_5)_2S]_2 + 2(C_2H_5)_2S \rightleftarrows 2[Pt(bph)(C_2H_5)_2S)_2]$, where the monomer serves as the reactive intermediate.

Electronic Spectra and Redox Behavior. The absorption features, absorption coefficients, and redox properties of the complexes are listed in Table I. The low-energy transitions in the 300–400-nm region were assigned as $d\pi \rightarrow \pi^*$(bph) transitions by analogy to previous transition assignments made for [Pt(bph)(bpy)].[6a] Higher energy transitions which ranged from 235 to 270 nm were also observed. The transitions were assigned as $\pi \rightarrow \pi^*$ intraligand transitions and have molar absorptivities greater than 10^4 M^{-1} cm^{-1}.

In the solvent window from +2 to −2 V, the complexes displayed one irreversible couple that ranged from 0.67 to 1.35 V, depending on the complex. Similar couples in other platinum compounds have been assigned to the oxidation Pt(II) → Pt(III).[20] The oxidized species then underwent reaction, presumably with solvent, to yield an unidentified product which was observed to plate out on the platinum electrode.

Luminescence Properties. The luminescence spectra of the complexes in solution are illustrated in Figure 1. The spectra show vibrational structure with maxima located at 493, 532, 569,

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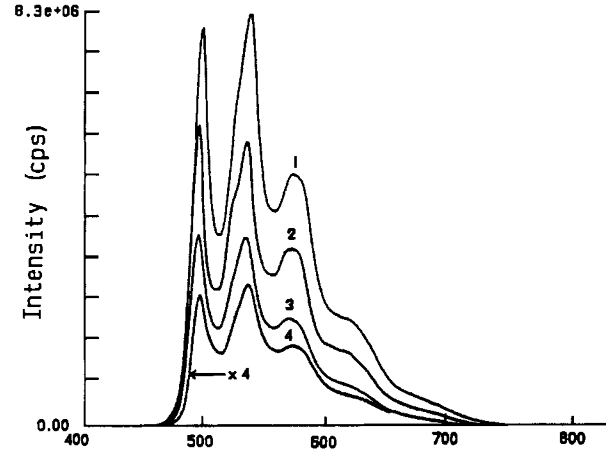

Figure 1. Corrected luminescence spectra of complexes in methylene chloride at room temperature (λ_{exc} = 355 nm): (1) [Pt(bpy)(en)]; (2) $[Pt(bpy)(CH_3CH)_2]$; (3) $[Pt(bph)(py)_2]$; (4) $[Pt(bph)(C_2H_5)_2S]_2$.

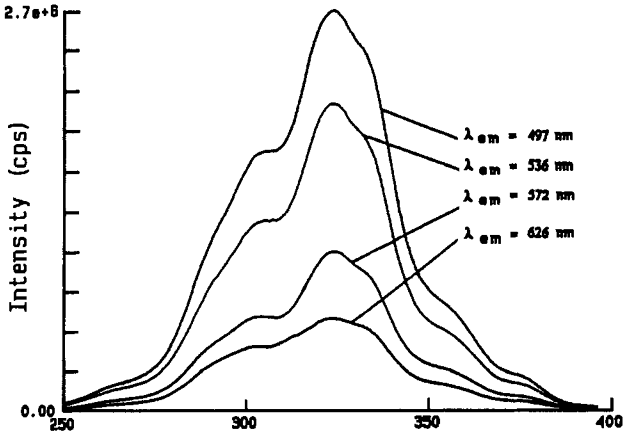

Figure 2. Dependence of excitation energy on emission wavelength for $[Pt(bph)(C_2H_5)_2S]_2$ in methylene chloride at 25 ± 1 °C.

and 620 nm. (There was a 4-nm red shift for the maxima of the sulfur-bridged dimer.) The vibrational progressions, which correspond to ring stretching modes, were approximately 1260 cm^{-1} apart. A solvent dependency study proved unfeasible due to the limited solubility of the complexes in various solvents but would probably not have provided additional insight as noted by the overlay in Figure 1, which consists of spectra for $[Pt(bph)(py)_2]$ in methylene chloride and $[Pt(bph)_2(CH_3CN)_2]$ in acetonitrile. Thus, on the basis of the similarity of the two spectra, it seems a reasonable conclusion that a change in solvent would not cause a significant deviation in either the position or the shape of the emission spectrum.

The luminescence spectra at 77 K were basically the same as those at room temperature. Little change in the shape or intensity from the room-temperature results was noted, except there was an approximate 4-nm blue shift of the spectra. In addition to the vibrational structure noted above, new structure was observed with progressions of about 300 cm^{-1}.

Excitation spectra of the complexes are illustrated in Figure 2. The spectra are basically the same with maxima located near 300 nm corresponding to the $d\pi \rightarrow \pi^*$(bph) transition. The excitation spectra were independent of the observation emission wavelength, indicating that emission occurs from one excited state in the complexes.

The high-energy emission maxima, excited-state lifetimes, and emission quantum yields are listed in Table II. The excited-state lifetimes, determined at room temperature, ranged from 3 µs for $[Pt(bph)(py)_2]$ to 14 µs for $[Pt(bph)(CH_3CN)_2]$. The emission lifetimes did increase somewhat upon lowering the temperature to 77 K, resulting in a range from 8 to 16 µs. The emission quantum yields were on the order of 0.16 ± 0.01, except for that of $[Pt(bph)(C_2H_5)_2S]_2$, which was 0.0077. This lowering may be due to the fact that it is a bimetallic complex and, in cases where luminescence has been observed for bimetallic complexes, the emission quantum yields have been lowered relative to their monometallic analogues,[21] presumably due to the heavy-atom effect, which provides additional low-energy vibronic pathways for excited-state energy loss.

Table II. Emission Energy Maxima, Emission Lifetimes, and Emission Quantum Yields[a]

	298 K		77 K		
complex	λ_{max},[b,c] nm	τ_0,[c,d] µs	λ_{max},[b,e] nm	τ_0,[d,e] µs	ϕ_{cm}[c,f]
$[Pt(bph)(C_2H_5S]_2$	497	10.5	490	12.2[g]	0.0077
$[Pt(bph)(CH_3CN)]_2$[h]	493	14.0	489	15.7[i]	0.18
[Pt(bph)(en)]	493	7.0	489	14.4[i]	0.16
$[Pt(bph)(py)_2]$	492	3.2	488	7.6[j]	0.15

[a] In methylene chloride unless otherwise noted; λ_{ex} = 355 nm. [b] Error in λ_{max} = ±1 nm. [c] T = 298 ± 1 K. [d] Error in τ_0 = ±10%. [e] T = 77 K. [f] Radiative quantum yield error = ±5%. [g] In methylene chloride–ethanol glass. [h] In acetonitrile. [i] In butyronitrile glass. [j] In isopentene–ethanol–diethyl ether–pyridine glass.

The luminescence was quenched in the presence of the Cl^- ion. The quenching process was a static one, suggesting that new species were formed by way of a dark reaction. Upon addition of Cl^- to $[Pt(bph)(py)_2]$ in methylene chloride, the $d\pi \rightarrow \pi^*$ transition decreased in intensity and broadened somewhat and then a slow reaction followed, as noted by a decrease in absorbance at 332 nm over a 4-h period. Details regarding this reaction are currently under investigation.

Electron-Transfer Quenching. The complexes behaved as powerful photoreductants and followed the behavior illustrated in eqs 1–3, where Q is an electron acceptor, k_q is the quenching

$$[Pt(bph)L_2] \xrightarrow{h\nu,\ 355\ nm} [Pt(bph)L_2]^* \qquad (1)$$

$$[Pt(bph)L_2]^* + Q \xrightarrow{k_q} [Pt(bph)L_2]^+ + Q^- \qquad (2)$$

$$[Pt(bph)L_2]^+ + Q^- \xrightarrow{k_{bet}} [Pt(bph)L_2] + Q \qquad (3)$$

rate constant, and k_{bet} is the back-electron-transfer rate constant. Estimates of excited-state redox potentials are given in Table I. The quencher used for reactions with $[Pt(bph)(CH_3CN)_2]$ and [Pt(bph)(en)] was methyl viologen ($E_{1/2}(MV^{2+/+})$ = –0.40 V).[22] The quencher[23] used for the reactions with $[Pt(bph)(C_2H_5)_2S]_2$ and $[Pt(bph)(py)_2]$ was *o*-dinitrobenzene ($E_{1/2}(Q^{0/-})$ = –0.81 V).[24] The results of Stern–Volmer studies based on luminescence quenching are presented in Table III. Stern–Volmer constants (K_{SV}) ranged from 19 690 to 56 107 M^{-1}. The quenching rate constants k_q, where $k_q = K_{SV}/\tau_0$,[25] were diffusion controlled. Laser flash photolysis provided spectroscopic evidence for MV^+ (λ_{max} = 605 nm, ϵ = 13 700 M^{-1} cm^{-1}).[26] The back-electron-transfer rate constant, k_{bet}, for the reaction of $[Pt(bph)(CH_3CN)_2]^+$ with MV^+ had a value of 1.5×10^{10} M^{-1} s^{-1}.

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Table III. Stern–Volmer Constants and Quenching Rate Constants[a]

complex	$10^{-4}K_{SV}$,[b] M^{-1}	k_q,[c] $M^{-1}\ s^{-1}$
$[Pt(bph)(C_2H_5)_2S]_2$[d]	1.3	9.6×10^{10}
$[Pt(bph)(CH_3CN)_2]$[e]	2.1	3.0×10^9
$[Pt(bph)(en)]$[e]	2.0	1.9×10^9
$[Pt(bph)(py)_2]$[d]	5.6	1.8×10^{10}

[a] $T = 23 \pm 1$ °C. [b] K_{SV} error = ±5%. [c] k_q error = ±10%. [d] *o*-Dinitrobenzene ($E_{1/2} = -0.81$ V); in methylene chloride. [e] Methyl viologen ($E_{1/2} = -0.42$ V); in acetonitrile.

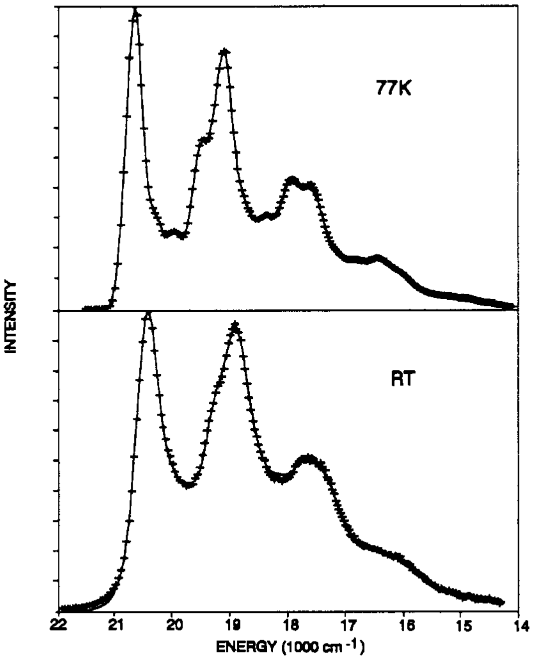

Figure 3. Corrected emission spectra of $[Pt(bph)(CH_3CN)_2]$ (+) in a 2-methyltetrahydrofuran glass at 77 K and in solution at room temperature. Spectra were calculated (—) using eq 4 and the spectral fitting parameters in Table IV.

Table IV. Emission Spectral Curve-Fitting Parameters in Butyronitrile at 77 and 298 K[a]

	[Pt(bph)(en)]		[(Pt(bph)($CH_3CN)_2$]		[Pt(bph)$(py)_2$]	
	77 K	298 K	77 K	298 K	77 K	298 K
E_{em}, cm^{-1}	20 660	20 408	20 700	20 450	20 620	20 325
E_{00}, cm^{-1}	20 660	20 430	20 700	20 455	20 630	20 370
$\hbar\omega_1$, cm^{-1}	1550	1570	1550	1575	1550	1560
S_1	0.90	0.90	0.91	0.86	0.83	0.98
$\hbar\omega_2$, cm^{-1}	1150	1150	1150	1150	1150	1150
S_2	0.60	0.62	0.60	0.60	0.59	0.62
$\hbar\omega_3$, cm^{-1}	710	720	720	720	715	715
S_3	0.25	0.29	0.26	0.27	0.19	0.27
$\hbar\omega_4$, cm^{-1}	375	375	375	375	375	375
S_4	0.28	0.28	0.28	0.28	0.28	0.28
$\Delta\bar{\nu}_{1/2}$, cm^{-1}	350	495	355	530	350	530

[a] Error limits are as follows: temperature, ±2 K; E_{00}, ±20 cm^{-1}; $\hbar\omega$, ±10 cm^{-1}; S, ±2%; $\Delta\bar{\nu}_{1/2}$, ±5%.

Table V. Kinetic Decay Parameters[a]

	[Pt(bph)(en)]	[Pt(bph)$(py)_2$]	[Pt(bph)$(CH_3CN)_2$]
k_1, s^{-1}	$(7.6 \pm 0.5) \times 10^4$	$(7.0 \pm 0.1) \times 10^4$	$(6.5 \pm 0.1) \times 10^4$
k_2, s^{-1}	$(1.1 \pm 0.8) \times 10^{13}$	$(3.8 \pm 0.5) \times 10^{11}$	$(2.5 \pm 0.1) \times 10^7$
ΔE_2, cm^{-1}	2490 ± 5	2280 ± 5	1220 ± 5

[a] In 2-MeTHF; T = 150–310 K; λ_{ex} = 355 nm.

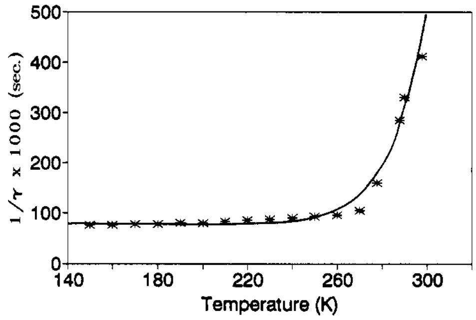

Figure 4. Plot of $1/\tau$ vs T for [Pt(bpy)(en)] in 2-methyltetrahydrofuran. The line is the result for the best fitting of eq 5 to the experimental points.

Emission Spectral Fitting Parameters. The corrected emission spectra of $[Pt(bph)(CH_3CN)_2]$ at 77 and 298 K are shown in Figure 3. Band shapes calculated from spectral curve-fitting parameters described by eq 4 are also illustrated in Figure 3. The

$$I(\hbar\omega) = I_\nu(\hbar\omega)/I_{00} - \sum_{\nu_i=0}\cdots\sum_{\nu_j=0}\{((E_{00} - \nu_i(\hbar\omega_i) - \ldots - V_j(\hbar\omega_j))/E_{00})^3 \times (S_i^{\nu_i}/\nu_i!) \times \ldots \times (S_j^{\nu_j}/\nu_j!) \times \exp[-(4 \times \ln 2)((\hbar\omega - E_{00} + \nu_i(\hbar\omega_i) + \ldots + \nu_j(\hbar\omega_j))/\Delta\bar{\nu}_{1/2})^2]\} \quad (4)$$

emission profiles were analyzed by a four-mode, temperature-dependent Franck–Condon analysis based on the parameters E_{00}, $S_{i\to j}$ (1, 2, 3, 4), $\hbar\omega_{i\to j}$ (1, 2, 3, 4), and $\Delta\bar{\nu}_{1/2}$. In the equation, E_{00} is the zero–zero energy, $S_{i\to j}$ and $\hbar\omega_{i\to j}$ are respectively the electronic–vibrational frequency modes that vary in energy from medium- to low-energy frequency vibrations, $\Delta\bar{\nu}_{1/2}$ is the full width at half-maximum for the individual vibronic contributors, and $\hbar\omega$ is the frequency of observation. In the emission spectrum, vibrational progressions can be seen at 77 K giving good initial estimates for $\hbar\omega$ values. The experimental spectra contained the theoretical features, but the resolution was less satisfactory, presumably due to the circular sample cells and the liquid nitrogen dewar windows. The data are collected in Table IV and can be summarized as follows. For the three complexes examined, parameters under the same heading have similar values. Thus, at 77 K, average values for the variables are as follows: E_{00} = 20 660 cm^{-1}, $\hbar\omega_1$ = 1550 cm^{-1}, $\hbar\omega_2$ = 1150 cm^{-1}, $\hbar\omega_3$ = 715 cm^{-1}, $\hbar\omega_4$ = 375 cm^{-1}, S_1 = 0.88, S_2 = 0.60, S_3 = 0.23, S_4 = 0.28, and $\Delta\bar{\nu}_{1/2}$ = 352 cm^{-1}. The similarity of values for a given variable is expected, since the excited electron resides in the π^* energy level of the bph ligand. The correlation of S values with $\hbar\omega$ values is also reasonable. As S decreases in magnitude, the emission intensity decreases and becomes distributed among a larger number of lower energy modes.

Temperature-Dependent Lifetime. Rate Constants for Excited-State Decay. Kinetic decay parameters are collected in Table V. Temperature-dependent lifetimes were fit to eq 5 in order to

$$(\tau(T))^{-1} = k_1 + k_2 \exp(-\Delta E_2/RT)/[1 + \exp(-\Delta E_2/RT)] \quad (5)$$

obtain k_1, k_2, and ΔE_2 values.[27] As illustrated in Figure 4, satisfactory fits of the data were obtained.

The experimental data can be summarized as follows. Within the series, k_1 is several orders of magnitude (3–11) smaller than k_2. The values for ΔE_2 change by about a factor of 2 from 1220 to 2490 cm^{-1}.

Discussion

The goal of the work was to study the photochemical and photophysical properties of a new series of complexes based on platinum(II). The key in the study was to fabricate molecules with high-energy emitting states. We took advantage of the fact that platinum(II) is known to form complexes with metal–carbon bonds,[28] which raise the energy of the ligand field state due to

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strong σ-bond interaction. This then provides a large energy spacing between the filled d orbitals and the dσ^* state and, hence, the opportunity to fill this void with unfilled orbitals on ligands capable of emitting energy when populated.

The biphenyl dianion was chosen as the chromophoric ligand for two reasons. First, it was possible to prepare 2,2′-dibromobiphenyl, convert it to 2,2′-dilithiobiphenyl by metal–halogen exchange, and then coordinate it to platinum(II) as a bidentate chelating ligand through the 2,2′-carbon atoms.[6a,13] Second, it contained an empty π^* energy level with energy in the spacing between the filled d and unfilled dσ^* states. Finally, to ensure that the filled d orbitals were the HOMO and the unfilled π^*(bph) orbitals were the LUMO, the other ligand(s) chosen for coordination to platinum(II) contained empty orbitals that were not located within the dd energy spacing.

Optical transitions near 330 nm were observed from the HOMO to the LUMO. The transitions were assigned as d$\pi \rightarrow \pi^*$(bph), in agreement with previously published results for similar compounds.[6,7] The energy of the transition remained relatively fixed for the series of complexes. However, redox potentials for the irreversible oxidation $[Pt(bph)L_2] \rightarrow [Pt(bph)L_2]^+$ did change by over 0.7 V in the series $[Pt(bph)(C_2H_5)_2S]_2$ > $[Pt(bph)(CH_3CN)_2]$ > $[Pt(bph)(py)_2]$ > $[Pt(bph)(en)]$. This variation and the fact that the optical transition remains at the same energy would indicate that the energies of the π^* levels change in concert with the energy of the ground state.

The emission spectra of the complexes shown in Figure 1 are basically identical to one another, indicating that emission occurs from a common origin. The highly resolved vibronic structure is typical of a ligand-centered process.[6b] In addition, the vibronic structure is similar to the behavior displayed by biphenyl itself, H_2bph, but is better resolved. In the past, better resolution was achieved by near planarity of the phenyl rings,[29] which is the expected result of bidentate coordination. On the basis of the clearly resolved band structure, the emission can be assigned to a ^{3}LC (ligand-centered) state with a small amount of MLCT character, which manifests itself in a lowering of radiative lifetimes from the millisecond time domain to the microsecond time scale. There is no experimental evidence for the presence of the ^{3}MLCT state, which presumably lies at higher energy than the ^{3}LC state. Similar observations have been reported for rhenium(I) tricarbonyl complexes.[30]

The results of emission spectral curve fitting of the complex give insight into excited-state structure. The results in Table IV obtained at room temperature and at 77 K were nearly the same, except at room temperature E_{00} was red-shifted 150–300 cm^{-1}, $\hbar\omega_1$ was red-shifted 10–25 cm^{-1}, and $\Delta\bar{\nu}_{1/2}$ was ~150 cm^{-1} larger. The vibrational progressions obtained from emission spectra were in agreement with data obtained from resonance Raman spectra for H_2bph and Hbph$^-$.[31,32] The displacements of the modes have been determined by normal-coordinate analysis.[33] The results indicate that vibrational coupling is largely distributed over the whole H_2bph molecule and atoms move preferentially all together.

Table VI. Comparison of Vibrational Frequencies for $[Pt(bph)L_2]$ Complexes to Those for H_2bph and Hbph$^-$

ν, cm^{-1}	$[Pt(bph)L_2]$[a]	Hbph$^-$ [b]	H_2bph[c]
1	1570	1587	1605
2	1150		1190
3	720	721	743
4	375	327	314

[a] This work. [b] Reference 28. [c] Dewar, M. J. S.; Trinajstic, N. *Czech. Chem. Commun.* **1970**, *35*, 3136.

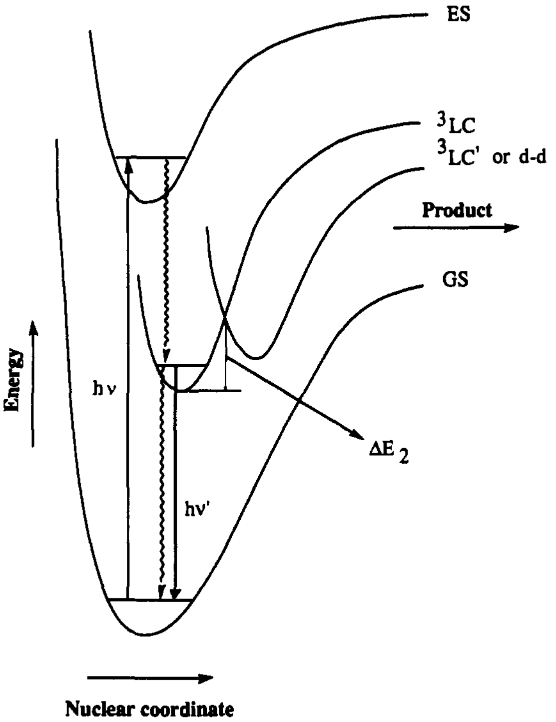

Figure 5. Proposed ordering of energy levels and representation of ΔE_2. ^{3}LC is the luminescing excited state.

A comparison of similar frequencies found from emission curve fitting to those reported from resonance Raman spectroscopy for H_2bph and Hbph$^-$ are listed in Table VI. We attempted to obtain resonance Raman spectra for $[Pt(bph)L_2]$ complexes as well.[34] Due to solubility limitations, only one mode located at 1584 cm^{-1} was observed for [Pt(bph)(en)] in methanol and 2-methyltetrahydrofuran and for $[Pt(bph)(CH_3CN)_2]$ in acetonitrile. The similarity of this value to the 1570 cm^{-1} frequency found by the emission curve-fitting routine is remarkable and suggests that the resonance Raman and luminescence techniques allow one to measure the same phenomenon.

One would expect the metal center to alter the energy of the modes. However, a comparison of the force constants for C(sp^2)–C(sp^2) (9.60 mdyn/Å), C(sp^2)–H (4.6 mdyn/Å),[35] and M–C (0.8 mdyn/Å)[36] would indicate that, to a first approximation, the bph ligand may vibrate almost as if the metal were not present. This is certainly the conclusion one makes when comparing the similarity of vibrational frequencies given for each mode in Table VI. The most likely exceptions to this postulate are the low energy modes, where the presence of metal–ligand vibrations are expected to contribute.[37]

The proposed ordering of energy levels based on absorption, emission, and temperature-dependent lifetime studies is shown in Figure 5. Upon absorption of energy, the ^{3}LC state is populated and undergoes radiative and nonradiative decay to the ground-state or energy transfer to another excited state by thermal means. The barrier to energy transfer, ΔE_2, varies from 1220 to 2490 cm^{-1}, depending on the complex. The physical significance of ΔE_2 and rates of energy transfer within the excited-state manifolds has been discussed for platinum(II) complexes[38] and rutheniu-

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m(II) heterocycles,[27,39,40] and a similar interpretation can be used here. In ruthenium(II) systems, ΔE_2 was attributed to the energy needed to thermally populate a ligand field state from the emitting state. The probe for the existence of the ligand field state was photosubstitution in the presence of the Cl^- ion. Unfortunately, $[Pt(bph)L_2]$ complexes underwent a dark reaction in the presence of the Cl^- ion. Thus, it was not possible to probe the nature of the thermally assessible state in the case of the $[Pt(bph)L_2]$ complexes. Tentatively, it has been assigned to a dd state; but it may also be a higher energy ^{3}LC state.

Recently, we reported[41] a correlation in a series of ruthenium(II) polypyridyl complexes between the preexponential factor (k) and the energy term (ΔE) obtained by using eq 5. This trend appears general, as noted here by the correlation between k_2 and ΔE_2. If k_2 is interpreted as the Arrhenius preexponential factor, then entropic arguments related to the higher density of vibrational states at the higher energy barrier crossover can be used to account for the trend.[41]

The energy gap between the emitting state and the ground state is approximately 2.6 eV in the $[Pt(bph)L_2]$ complexes. Typical values for ruthenium(II), osmium(II), and rhenium(I) are less than 2.0 eV.[1] Energy gaps in the 2.6-eV regime have been obtained for a few other complexes. Some examples are iridium phenylpyridine complexes,[42] platinum dicyano complexes,[11,12] and some rhodium complexes.[43] Depending on ground-state redox potentials, rather substantial excited-state redox potentials can be achieved. For $[Pt(bph)L_2]$ complexes, the approximate $[Pt(bph)L_2]^{+/0*}$ potential was −1.5 V. In conclusion, the design of molecules with large emission energy gaps may be useful for energy conversion studies when a large driving force is necessary to effect oxidation or reduction of substrates.[44]

Acknowledgment. We thank the Office of Basic Energy Science of the Department of Energy under Grant No. DE-FG05-84ER13263 for support, Johnson Matthey for the platinum source compounds on loan, and Lithco, Inc., a Division of FMC, for the alkyllithium compounds.

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