Multiple-State Emission and Excited-State Dynamics of CpRe(CO)₂L (L = 3-Benzoylpyridine and 4-Benzoylpyridine) Complexes in Fluid and Glassy Solutions

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Electronic absorption, emission and excitation spectra, and emission lifetimes have been recorded from CpRe-(CO)₂(3-Bzpy) and CpRe(CO)₂(4-Bzpy) (3-Bzpy = 3-benzoylpyridine, 4-Bzpy = 4-benzoylpyridine) complexes in fluid solution at 218–298 K and in glassy 2-MeTHF (2-MeTHF = 2-methyltetrahydrofuran) at 77 K. Analogous data have also been determined for the corresponding free ligands. The results obtained reveal the nature of the lowest electronically excited states and the mechanisms of the photophysical deactivation processes in these systems. The CpRe(CO)₂(3-Bzpy) molecule is found to exhibit multiple emission from triplet-centered n,π^* intraligand (^{3}IL) and metal-to-ligand charge-transfer (^{3}MLCT) levels. In fluid solution these two emitting states establish a thermal equilibrium; luminescence data obtained from temperatures between 218 and 298 K are fitted to a Boltzmann model yielding an energy separation between the participating levels of 665 cm^{-1}. In the frozen 2-MeTHF glass at 77 K these ^{3}IL and ^{3}MLCT states are no longer thermally equilibrated and emit independently. Contrastingly, only one emission feature is observed for CpRe(CO)₂(4-Bzpy) at both room and low temperatures; this is assigned to a lowest energy ^{3}MLCT state. The striking differences between the photophysical behaviors of these two molecules are discussed in terms of the electronic characteristics of the 3-Bzpy and 4-Bzpy molecules and possible geometrical differences of the excited states involved.

Introduction

In order to obtain a full understanding of a molecule's photochemistry it is necessary to characterize its lowest-lying electronically-excited states and photophysical deactivation mechanisms. Emission spectroscopic techniques often present a highly sensitive and effective way to identify the lowest-energy excited states and their degradation pathways.[1] Over the past few years there has been much attention paid to transition-metal complexes that exhibit optically induced multiple-state emission and the photophysical processes that give rise to this unusual phenomenon. There are now several metal complexes recognized to be multiply emissive in either frozen glassy[2] or fluid solution[3] conditions. Typically, the participating excited-state levels in these systems have been determined to be thermally equilibrated under fluid conditions and the dynamic behavior between these levels has been rationalized with the adoption of modified Boltzmann population models.[3,4]

Among organometallic species simultaneous multiple emission has been observed from a series of *fac*-[XRe(CO)₃L₂] (X = Cl,

Br, I; L = 4-Phpy, 4,4'-bpy, 3-Bzpy, 4-Bzpy)[5] and *fac*-[SRe-(CO)₃L]⁺ (S = CH₃CN, PhCN, py, pip; L = phen, biquin)[6] complexes. At room temperature the emission spectra of these complexes are dominated by triplet-centered metal-to-ligand charge-transfer (^{3}MLCT) emission. However, at 77 K these molecules also exhibit ^{3}(n → π^*) or ^{3}(π → π^*) intraligand (^{3}IL) emissions. The M(CO)₄(α,α'-diimine) (M = Cr, Mo, W; α,α'-diimine = bpy, phen, or a derivative ligand) system is also recognized to be multiply emissive, even displaying dual emission features under room-temperature solution conditions.[7] The photophysics of these complexes are fairly complicated and have been studied in some detail; the participating excited states are understood to involve a nonequilibrated ligand field (^{3}LF) level and a lowest lying thermally equilibrated ^{3}MLCT manifold.[7d] Recently, nonequilibrated multiple-state emission has been characterized from CpRe(CO)₂L (Cp = η⁵-C₅H₅; L = py, 4-Phpy) complexes and the excited-state deactivation mechanisms have been rationalized on a ^{3}MLCT/^{3}LF model.[8]

In this article we report on the results obtained by following a systematic photophysical study of CpRe(CO)₂L complexes, where L = 3-benzoylpyridine (3-Bzpy) and 4-benzoylpyridine (4-Bzpy). Our experimental observations indicate that these complexes exhibit an intricate multiple-state emission system but that they differ substantially from the previously reported CpRe-(CO)₂L derivatives in that intraligand states are also involved in the excited-state decay pathway. Moreover, we find that the photophysical properties are strikingly different for these two complexes and a comparison of the emission data provides valuable information on the precise roles of the lowest-lying ^{3}IL and

(1) Lees, A. J. *Chem. Rev.* 1987, 87, 711.
(2) (a) DeArmond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* 1981, 36, 325. (b) Sullivan, B. P.; Abruna, H.; Finklea, H. O.; Salmon, D. J.; Nagle, J. K.; Meyer, T. J.; Sprintschnik, H. *Chem. Phys. Lett.* 1978, 58, 389. (c) Rader, R. A.; McMillin, D. R.; Buckner, M. T.; Matthews, T. G.; Casadonte, D. J.; Lengel, R. K.; Whittaker, S. B.; Darmon, L. M.; Lytle, F. E. *J. Am. Chem. Soc.* 1981, 103, 5906. (d) Martin, M.; Krogh-Jespersen, M.-B.; Hsu, M.; Tewksbury, J.; Laurent, M.; Viswanath, K.; Patterson, H. *Inorg. Chem.* 1983, 22, 647. (e) Belser, P.; von Zelewsky, A.; Juris, A.; Barigelletti, F.; Balzani, V. *Chem. Phys. Lett.* 1984, 104, 100. (f) Segers, D. P.; DeArmond, M. K.; Grutsch, P. A.; Kutal, C. *Inorg. Chem.* 1984, 23, 2874. (g) Casadonte, D. J.; McMillin, D. R. *J. Am. Chem. Soc.* 1987, 109, 331. (h) Casadonte, D. J.; McMillin, D. R. *Inorg. Chem.* 1987, 26, 3950. (i) Blakley, R. L.; DeArmond, M. K. *J. Am. Chem. Soc.* 1987, 109, 4895.
(3) (a) Watts, R. J. *Inorg. Chem.* 1981, 20, 2302. (b) Kirchhoff, J. R.; Gamache, R. E.; Blaskie, M. W.; Del Paggio, A. A.; Lengel, R. K.; McMillin, D. R. *Inorg. Chem.* 1983, 22, 2380. (c) Nishizawa, M.; Suzuki, T. M.; Sprouse, S.; Watts, R. J.; Ford, P. C. *Inorg. Chem.* 1984, 23, 1837. (d) Zulu, M. M.; Lees, A. J. *Inorg. Chem.* 1989, 28, 85.
(4) Kemp, T. J. *Prog. React. Kinet.* 1980, 10, 301.

(5) (a) Giordano, P. J.; Fredericks, S. M.; Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* 1978, 100, 2257. (b) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* 1979, 101, 2888.
(6) Fredericks, S. M.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* 1979, 101, 7415.
(7) (a) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* 1983, 22, 572. (b) Servaas, P. C.; van Dijk, H. K.; Snoeck, T. L.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* 1985, 24, 4494. (c) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* 1986, 25, 1354. (d) Rawlins, K. A.; Lees, A. J. *Inorg. Chem.* 1989, 28, 2154.
(8) (a) Glezen, M. M.; Lees, A. J. *J. Am. Chem. Soc.* 1988, 110, 6243. (b) Glezen, M. M.; Lees, A. J. *J. Am. Chem. Soc.* 1989, 111, 6602.

^{3}MLCT levels in the excited-state dynamic processes. The photophysics of CpRe(CO)$_2$(3-Bzpy) and CpRe(CO)$_2$(4-Bzpy) are investigated in detail under both room- and low-temperature solution environments.

Experimental Section

Materials. Rhenium pentacarbonyl chloride (Pressure Chemical), 3-Bzpy (Aldrich), and 4-Bzpy (Aldrich) were purified by repeated sublimations under reduced pressure. Cyclopentadienylthallium (Aldrich) was obtained in high purity and used as received. Tetrahydrofuran (THF) was obtained as reagent grade (Fisher) and was first purified by passage through a 2 × 10-cm column of activated alumina to remove peroxides and then rigorously dried by distillation over LiAlH$_4$ (Aldrich). This was stored under an inert atmosphere prior to use. The solvent 2-methyltetrahydrofuran (2-MeTHF) was obtained as spectroscopic grade (Aldrich), and it was further dried and degassed according to a standard literature procedure.[9] The solvents used in the emission experiments were obtained as photrex grade (J. T. Baker) and were repeatedly distilled to remove emitting or quenching impurities. Nitrogen gas used for purging was dried and deoxygenerated according to a previously published method.[10]

Syntheses. The CpRe(CO)$_3$ parent complex was prepared by refluxing rhenium pentacarbonyl chloride (1 g) and cyclopentadienylthallium (3.72 g) in hexane (300 mL) for 24 h analogous to a literature procedure.[11] A white product was obtained following filtration of the reflux mixture and rotary evaporating the solvent. This material was purified by repeated sublimations under reduced pressure and obtained in 91% yield (lit. yield 87%).[12] IR of CpRe(CO)$_3$: in dichloromethane, ν(CO) 2021 (vs), 1924 (vs) cm^{-1}; in carbon tetrachloride, ν(CO) 2028 (vs), 1936 (vs) cm^{-1} (lit. in isooctane, 2028, 1938 cm^{-1}).[13] Mp of CpRe(CO)$_3$: 111–112 °C (lit. mp 112 °C).[12] The CpRe(CO)$_2$(3-Bzpy) and CpRe(CO)$_2$(4-Bzpy) complexes were prepared via thermal reaction of the prior photoproduced THF adduct, CpRe(CO)$_2$(THF), with an excess amount of the appropriate ligand according to a previously described procedure with minor modifications.[13] Typically, a deoxygenated THF solution (200 mL) of 10^{-3} M CpRe(CO)$_3$ was irradiated for 2 h with a 200-W medium-pressure Hg lamp to initially form the THF adduct. Excess free ligand (5 × 10^{-3} M) was subsequently added, and the THF adduct was allowed to react for 3 h in the dark to form the pyridino product. IR and UV–visible spectra were recorded throughout these reactions to monitor product formation. In each case the product was obtained by rotary evaporating the solvent and purification by column chromatography on silica gel; initial elution with hexane removed unreacted CpRe(CO)$_3$, and then elution with dichloromethane/hexane (5:1 v/v) removed a red product in yields of 25–30%. The CpRe(CO)$_2$L complexes were further purified by recrystallization from a hexane/diethyl ether (4:1 v/v) solution. The products are fairly air-stable but were generally kept under N$_2$ in the dark. IR of CpRe(CO)$_2$(3-Bzpy): in dichloromethane, ν(CO) 1904 (vs), 1830 (vs) cm^{-1}; in carbon tetrachloride, ν(CO) 1919 (vs), 1849 (vs) cm^{-1} (lit. in isooctane, 1926, 1861 cm^{-1}).[13] IR of CpRe(CO)$_2$(4-Bzpy): in dichloromethane, ν(CO) 1906 (vs), 1834 (vs) cm^{-1}; in carbon tetrachloride, ν(CO) 1920 (vs), 1852 (vs) cm^{-1} (lit. in isooctane, 1928, 1866 cm^{-1}).[13]

Equipment and Procedures. Infrared spectra were recorded on Perkin-Elmer 283B and Nicolet 20SXC FTIR spectrometers as solutions in a NaCl cell of 1-mm path length. The reported data are considered accurate to ±1 cm^{-1}. Electronic absorption spectra were obtained on Hewlett-Packard 8450A and Perkin-Elmer 559A UV-visible spectrometers. The reported maxima are considered accurate to ±2 nm.

Emission and excitation spectra were recorded on a SLM 8000/8000S dual-monochromator spectrometer which incorporates a photomultiplier-based photon-counting detector. A red-sensitive Hamamatsu R928 photomultiplier tube was used in these measurements, and the reported emission band maxima are uncorrected for wavelength variations in the detector response. For each complex the resultant emission band maxima were found to be reproducible to ±2 nm. Excitation spectra were recorded from samples that were optically dilute ($A < 0.05$) throughout the spectral region scanned and were corrected for wavelength variations in the exciting-lamp intensity. Following this correction, excellent agreements were obtained between the excitation and absorption spectra for the known

standards quinine sulfate and 1,2-benzanthracene under similar optically dilute conditions.[14] Excitation spectra were found to be reproducible to ±4 nm.

Emission lifetimes were recorded on a Photochemical Research Associates (PRA) System 3000 time-correlated pulsed single-photon counting apparatus.[15] Samples were excited with light from a PRA 510 nitrogen flashlamp transmitted through an Instruments SA Inc. H-10 monochromator, and emission was detected at 90° via a second H-10 monochromator onto a thermoelectrically cooled red-sensitive Hamamatsu R955 photomultipler tube. The resulting photon counts were stored on a Tracor Northern 7200 microprocessor-based multichannel analyzer. The instrument response function was subsequently deconvoluted from the emission data to yield an undisturbed decay which was fitted by an iterative least-squares procedures on an IBM-PC. In each case single exponential fits were obtained; the reported lifetimes were found to be reproducible to the quoted errors of ±10% over a least three measurements.

In all the emission experiments the sample solutions were filtered through 0.22-μm Millipore filters and then deoxygenated by N$_2$-purging for 15 min prior to taking readings. Solutions were contained in 1-cm square quartz cells. IR and UV–visible spectra were checked before and after irradiation to monitor possible sample degradation. For studies at or near room temperature the solutions were controlled to ±0.1 K by circulating a thermostated ethylene glycol mixture through a jacketed cell holder placed in the emission apparatus.

Absorption and emission measurements at temperatures below room temperature were performed with an Oxford Instruments DN1704K variable-temperature liquid-N$_2$-cooled cryostat fitted with synthetic sapphire inner windows and quartz outer windows. Samples were contained in a fused-quartz 1-cm path length cell and were rigorously deaerated by successive freeze–pump–thaw cycles prior to taking measurements. The temperature of the solution within the cryostat was maintained to ±0.2 K with an Oxford Instruments 3120 controller.

Results

Figure 1 and Table I depict electronic absorption spectral results obtained from the CpRe(CO)$_2$L (L = 3-Bzpy and 4-Bzpy) complexes and the corresponding free ligands in isooctane at room temperature. Each of the free ligands exhibits two distinct absorption features: an intense band ($\epsilon > 10\,000$ M^{-1} cm^{-1}) centered at 254 nm (3-Bzpy) or 258 nm (4-Bzpy) and a much weaker band ($\epsilon \sim 100$ M^{-1} cm^{-1}) centered at 341 nm (3-Bzpy) or 334 nm (4-Bzpy). Moreover, the higher energy bands of both free ligands are observed to red-shift by apporximately 1240–1450 cm^{-1} on changing to the more polar dichloromethane solvent, whereas the lower energy band concomitantly blue-shifts by approximately 590–870 cm^{-1} in this solution (see Table I). Significantly, the long wavelength absorption feature of 3-Bzpy in isooctane solution exhibits vibrational structure with the bands being separated by an average value ($\Delta\nu_{av}$) of 1102 cm^{-1} (see Table II). In contrast, the corresponding lower energy band of 4-Bzpy was not found to exhibit any vibrational structure.

Electronic absorption spectra of the CpRe(CO)$_2$L complexes are dominated by intense bands in the UV and visible regions (see Figure 1a and Table I). The higher energy bands (centered at 258 nm for CpRe(CO)$_2$(3-Bzpy) and 264 nm for CpRe(CO)$_2$-(4-Bzpy) in isooctane) are approximately at the same energy positions as the corresponding free ligands, and they exhibit similar band intensities and solvent sensitivities as the free ligands. The lower energy bands are observed as broad envelopes in the visible region, and in each case they apparently comprise more than one absorption feature with the presence of a distinct shoulder at the low-energy side of the main absorption band. It is noticeable that the long wavelength absorption features of the 4-Bzpy derivative are considerably more red-shifted than the corresponding 3-Bzpy derivative (see Figure 1 and Table I). Moreover, the energy positions of these visible transitions are dependent on both solvent and temperature/environment changes. Figure 2

(9) Gordon, A. J.; Ford, R. A. *The Chemist's Companion, A Handbook of Practical Data, Techniques, and References*; Wiley: New York, 1972.
(10) Schadt, M. J.; Gresalfi, N. J.; Lees, A. J. *Inorg. Chem.* **1985**, *24*, 2942.
(11) King, R. B.; Reimann, R. H. *Inorg. Chem.* **1976**, *15*, 179.
(12) Fischer, E. O.; Fellman, W. *J. Organomet. Chem.* **1963**, *1*, 191.
(13) Giordano, P. J.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 160.

(14) Berlman, I. B. *Handbook of Fluorescence of Aromatic Molecules*, 2nd ed.; Academic Press: New York, 1971.
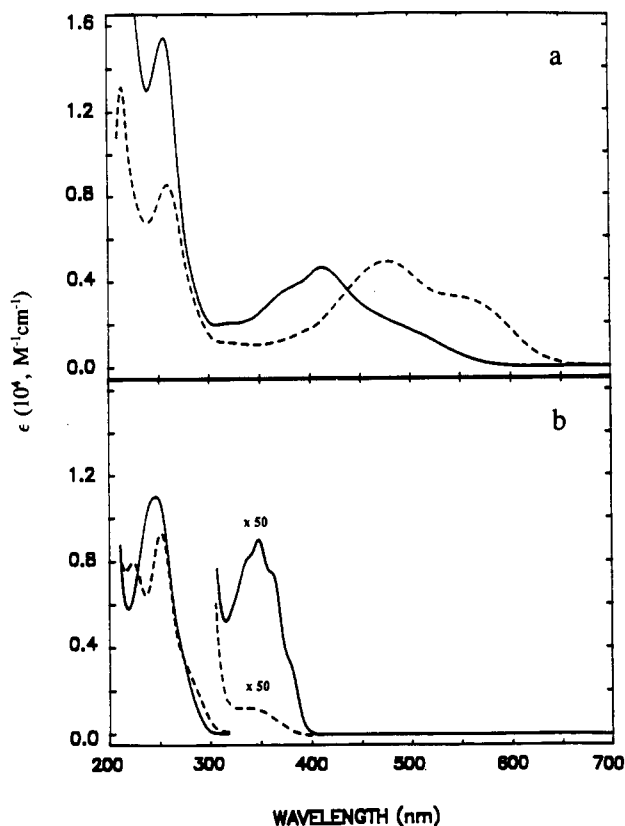(15) O'Connor, D. V.; Phillips, D. *Time-Correlated Single Photon Counting*; Academic: London, 1984.

Figure 1. Electronic absorption spectra of (a) $CpRe(CO)_2$(3-Bzpy) (—) and $CpRe(CO)_2$(4-Bzpy) (- - -) and (b) 3-Bzpy (—) and 4-Bzpy (- - -) free ligands in isooctane at 293 K.

Figure 2. Electronic absorption spectra of (a) $CpRe(CO)_2$(3-Bzpy) and (b) $CpRe(CO)_2$(4-Bzpy) in dichloromethane (—), benzene (- - -), and isooctane (- - - -) at 293 K. Spectra are drawn to make absorbances equal at the maxima.

Table I. Electronic Absorption Spectral Data for the 3-Bzpy and 4-Bzpy Free Ligands and the Corresponding $CpRe(CO)_2$L Complexes in Various Solvents at 293 K

compd	solvent	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
3-Bzpy	dichloromethane	254 (13 800), 341 (137)
	isooctane	245 (11 000), 384 (180)
4-Bzpy	dichloromethane	258 (12 100), 334 (126)
	isooctane	250 (9300), 344 (121)
$CpRe(CO)_2$(3-Bzpy)	dichloromethane	258 (13 200), 376 (4580), 450[a]
	benzene	254 (14 100), 400 (4880), 476[a]
	isooctane	248 (15 600), 412 (4780), 510[a]
$CpRe(CO)_2$(4-Bzpy)	dichloromethane	264 (11 800), 446 (5340), 518[a]
	benzene	260 (10 300), 466 (4680), 530[a]
	isooctane	256 (8520), 476 (4870), 555[a]

[a] Observed as a shoulder.

Table II. Vibrational Structure on the Electronic Absorption Spectrum of the 3-Bzpy Free Ligand in Solution at 293 K

compd	solvent (temp, K)	λ_{max}, nm	ν, cm^{-1}	$\Delta\nu$ ($\nu^n - \nu^{n+1}$), cm^{-1}
3-Bzpy	isooctane (293)	324	30 864	1102
		336	29 762	1026
		348	28 736	1112
		362	27 624	1169
		378	26 455	

and Table I depicts electronic absorption spectra observed from $CpRe(CO)_2$(3-Bzpy) and $CpRe(CO)_2$(4-Bzpy) in various solvents at room temperature. These spectra illustrate that the lowest energy bands substantially blue-shift as the solvent is changed to a more polar (or polarizable) medium. In addition, when a 2-MeTHF solution is cooled from 293 to 77 K and becomes a rigid glass, there is a noticeable blue-shift in the visible absorption band of these complexes; this shift is especially pronounced for the long-wavelength shoulder. Figure 3 presents results obtained for the $CpRe(CO)_2$(3-Bzpy) complex.

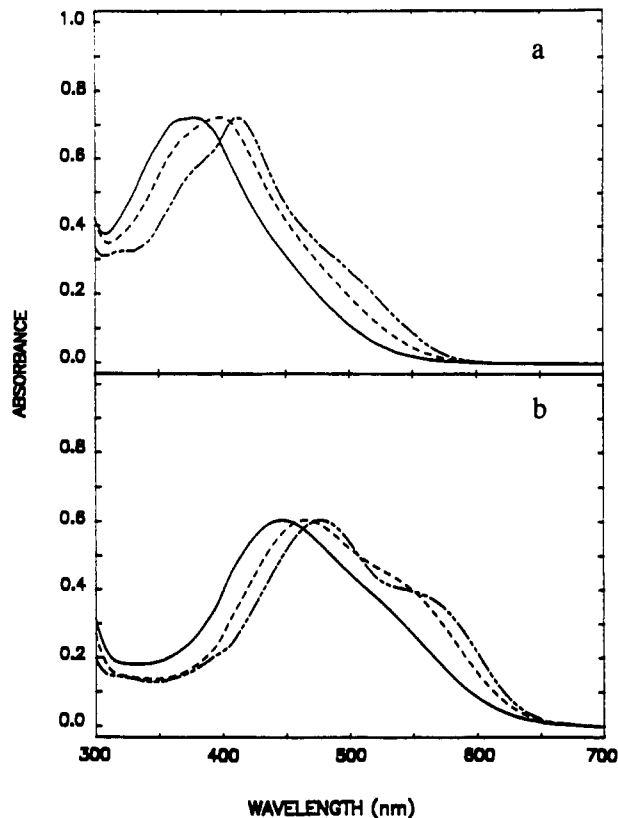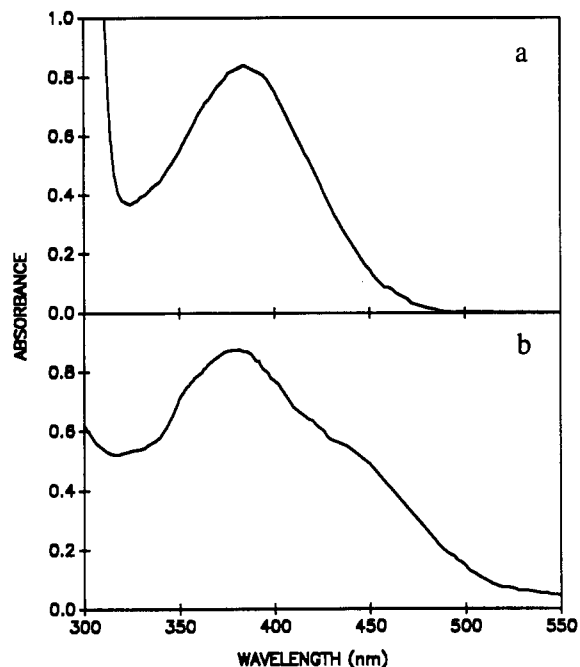**Figure 3.** Electronic absorption spectra of $CpRe(CO)_2$(3-Bzpy) in 2-MeTHF at (a) 293 and (b) 77 K. The low-temperature spectrum is not corrected for solvent contraction.

Emission spectra have been recorded from the free ligands in deoxygenated solutions at room temperature and in deaerated 2-MeTHF glassy solutions at low temperature. Figures 4 and 5 illustrate emission spectra obtained from 3-Bzpy and 4-Bzpy in dichloromethane at 293 K and in 2-MeTHF at 77 K following excitation into their lowest energy absorption bands. Each of these free ligands exhibit prominent vibrational structure at both
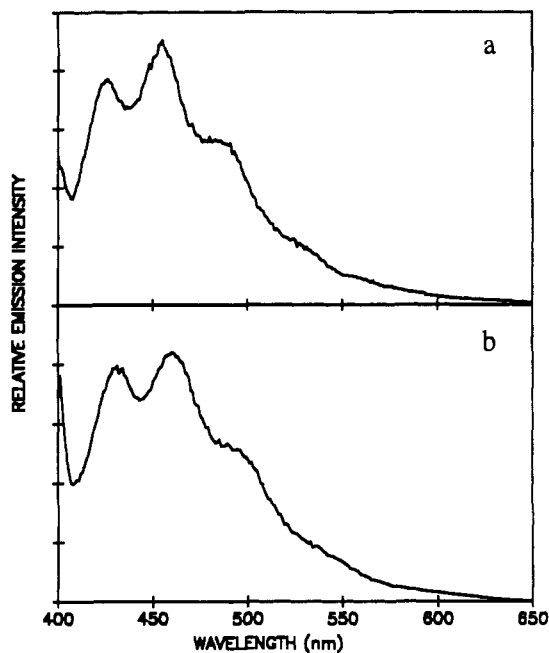
Figure 4. Emission spectra of (a) 3-Bzpy and (b) 4-Bzpy free ligands in deoxygenated dichloromethane at 293 K. Excitation wavelengths are 340 and 350 nm, respectively.
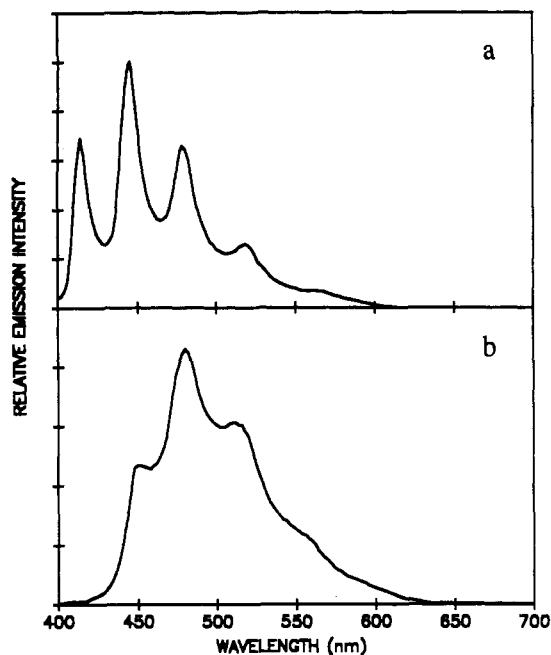

Figure 5. Emission spectra of (a) 3-Bzpy and (b) 4-Bzpy free ligands in deaerated 2-MeTHF at 77 K. Excitation wavelengths are 340 and 350 nm, respectively.

Table III. Vibrational Structure on the Emission Spectra of the 3-Bzpy and 4-Bzpy Free Ligands in Solution at 293 and 77 K

compd	solvent (temp, K)	λ_{max}, nm	ν, cm^{-1}	$\Delta\nu$ $(\nu^n - \nu^{n+1})$, cm^{-1}
3-Bzpy	dichloromethane (293)	420	23 810	1686
		452	22 124	1632
		488	20 492	
		532	18 797^a	
4-Bzpy	dichloromethane (293)	436	22 936	1338
		463	21 598	1437
		496	20 161	
		534	18 727^a	
3-Bzpy	2-MeTHF (77)	415	24 096	1573
		444	22 523	1602
		478	20 921	1541
		516	19 380	1555
		561	17 825	
4-Bzpy	2-MeTHF (77)	453	22 075	1285
		481	20 790	1297
		513	19 493	1344
		551	18 149	
		595	16 807^a	

^{a} Observed as a weak shoulder and not used in determining $\Delta\nu$.
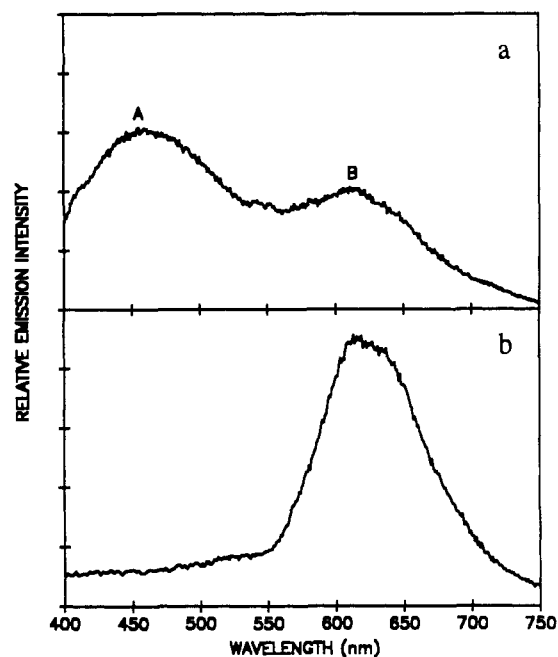
Figure 6. Emission spectra of (a) CpRe(CO)₂(3-Bzpy) and (b) CpRe-(CO)₂(4-Bzpy) in deoxygenated dichloromethane at 293 K. Excitation wavelengths are 360 and 400 nm, respectively.

room and low temperature; these data are summarized in Table III. Importantly, the emission from the 3-Bzpy free ligand gives rise to a much larger average vibrational separation at either room temperature ($\Delta\nu_{av}$ = 1659 cm⁻¹) or low temperature ($\Delta\nu_{av}$ = 1568 cm⁻¹) compared to that for the 4-Bzpy molecule at room temperature ($\Delta\nu_{av}$ = 1388 cm⁻¹) and low temperature ($\Delta\nu_{av}$ = 1309 cm⁻¹). Furthermore, when the solvent is changed to the less polar isooctane medium, the room temperature emission spectra reveal that these structured bands are somewhat red-shifted for 3-Bzpy [λ_{max} = 427, 455, 492, 595 (sh)] but slightly blue-shifted for 4-Bzpy [λ_{max} = 430, 459, 492, 582 (sh)] compared to those observed in dichloromethane (see Table III). Excitation spectra recorded from the free ligands in dichloromethane and isooctane solutions at 293 K exhibit congruence with the lowest-energy
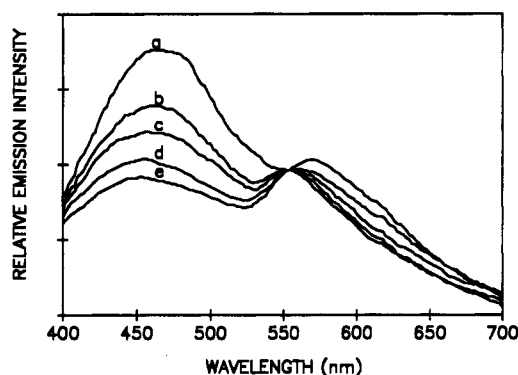
absorption bands, confirming that the emission in each case originates from the lowest-lying excited state.

Figure 6 shows emission spectra that have been recorded from the CpRe(CO)₂(3-Bzpy) and CpRe(CO)₂(4-Bzpy) complexes in deoxygenated dichloromethane at 293 K. Obviously, these spectra are strikingly different: two emission bands are observable centered at 455 and 610 nm from the CpRe(CO)₂(3-Bzpy) complex and only one emission feature is observable centered at 625 nm from the CpRe(CO)₂(4-Bzpy) complex. These emission spectra were found to be reproducible for different preparations of the CpRe(CO)₂L complexes, ruling out emission from common sample or solvent impurities. Additionally, no emission was observed from the parent CpRe(CO)₃ complex under these excitation conditions, consistent with our earlier report.[8b] Emission from a photochemically-produced impurity (such as another CpRe(CO)₂L derivative or a rhenium dimeric species) can be excluded on the basis that the emission spectral distribution is not affected by varying the irradiation time during which these measurements were performed. Significantly, the dual luminescence spectral distribution of CpRe(CO)₂(3-Bzpy) was ex-

Table IV. Emission Spectral Data for CpRe(CO)₂L (L = 3-Bzpy and 4-Bzpy) Complexes in Solution at 293 and 77 K

| compd	solvent (temp, K)	emission[a]	
		λ_{max}, nm	τ, μs[b]
CpRe(CO)₂(3-Bzpy)	dichloromethane (293)	455	5.2 (±0.5)
		610	5.2 (±0.5)
	isooctane (293)	458	5.4 (±0.5)
		647	5.4 (±0.5)
	2-MeTHF (77)	414, 445, 478	>300
		600[c]	8.6 (±0.9)
CpRe(CO)₂(4-Bzpy)	dichloromethane (293)	625	3.5 (±0.4)
	2-MeTHF (77)	607	8.7 (±0.9)

[a] Emission data recorded following excitation between 340 and 400 nm. [b] Lifetimes determined at the emission maxima. [c] Observed as a shoulder.

Figure 8. Emission spectra of (a) CpRe(CO)₂(3-Bzpy) and (b) CpRe-(CO)₂(4-Bzpy) in deaerated 2-MeTHF at 77 K. Excitation wavelengths are 350 (—) and 400 nm (- - -) for CpRe(CO)₂(3-Bzpy) and 390 nm (—) for CpRe(CO)₂(4-Bzpy).

Figure 7. Emission spectra of CpRe(CO)₂(3-Bzpy) in deoxygenated dichloromethane at (a) 218, (b) 238, (c) 258, (d) 278, and (e) 298 K. Excitation wavelength is 360 nm in each case.

amined in fluid solution throughout the temperature range 218–298 K and was determined to not be affected by variations in the excitation wavelength over the 340–400-nm region, confirming that the complex is a true multiple-state emitter and the emission being observed is not just from an impurity species. For convenience, the two emission features from this complex are hereafter denoted as bands A and B, designated in order of decreasing energy position (see Figure 6a). The single emission band recorded from CpRe(CO)₂(4-Bzpy) is also uninfluenced by variations in the excitation wavelength over the 340–400-nm region, and it is notable that this band is slightly red-shifted compared with band B of the CpRe(CO)₂(3-Bzpy) derivative.

Solvent and temperature changes are seen to affect the emission spectral results (see Table IV). Band B of the CpRe(CO)₂-(3-Bzpy) complex and the single band of the CpRe(CO)₂-(4-Bzpy) complex are observed to be solvent dependent, exhibiting solvent shifts parallel to those noted in the absorption spectra. In contrast, the energy position of band A of the former complex is not significantly affected by solvent changes. When the temperature of a solution of CpRe(CO)₂(3-Bzpy) in deoxygenated dichloromethane is lowered from 298 to 218 K, there are discernible changes in the intensities of the two emission bands A and B (see Figure 7). Upon cooling, the intensity of band A increases substantially and the intensity of band B diminishes slightly. Furthermore, it can be noted that an isoemissive point (at 553 nm) is retained throughout this temperature sequence.

Excitation spectra have been recorded while monitoring the emission at each of the maxima of bands A and B of CpRe-(CO)₂(3-Bzpy) in deoxygenated dichloromethane and isooctane solutions at 293 K. In each case the obtained excitation data reveal two maxima at 360 and 395 nm and an overall broad spectrum in the 320–450-nm region which shows fairly good congruence with the intense absorption band envelope. Importantly, the excitation spectral distribution does not change on
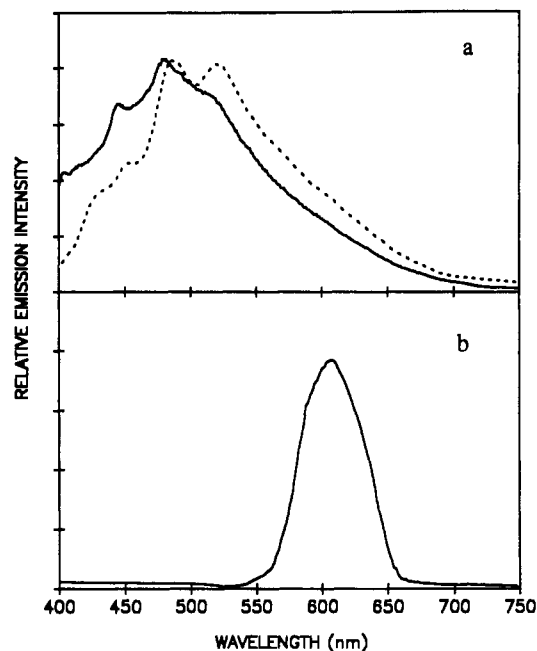
varying the wavelength at which the emission is monitored throughout the dual-band luminescence spectrum. In comparison, the CpRe(CO)₂(4-Bzpy) complex exhibits a broad excitation envelope in the 300–480-nm region with a main feature centered at ~390 nm; this spectrum also does not alter when the monitoring wavelength is varied throughout the single emission band.

Low-temperature emission data have been obtained from the two CpRe(CO)₂L complexes in frozen 2-MeTHF glasses at 77 K (see Figure 8). For each complex the emission intensity recorded at 77 K was observed to increase at least 10-fold compared to the spectra obtained at room temperature. The CpRe(CO)₂(3-Bzpy) complex gives rise to a structured emission spectrum with a maximum centered at 478 nm (see Figure 8a); both the vibrational progression and energy position of this band are similar to those of the free 3-Bzpy ligand (see Figure 5a), although the band structure for the organometallic complex is not as clearly resolved. Additionally, the low-temperature spectrum of CpRe(CO)₂(3-Bzpy) now reveals an excitation wavelength dependence; the relative intensity of the emission component at lower energy becomes more intense on excitation at longer wavelength (see Figure 8a). In sharp contrast, the CpRe(CO)₂(4-Bzpy) complex at low temperature exhibits an unstructured emission which is centered at 607 nm (see Figure 8b); this emission feature is not shifted on varying the excitation wavelength throughout the 340–400-nm region.

Emission lifetimes have been measured for the CpRe(CO)₂L complexes at both room and low temperatures (see Table IV). Importantly, for the CpRe(CO)₂(3-Bzpy) derivative in deoxygenated dichloromethane solution at 293 K the emission lifetimes obtained from both the upper energy (band A) and lower energy (band B) features are identical at 5.2 (±0.5) μs. Similar observations are made in deoxygenated isooctane (see Table IV). The single emission band observed from the CpRe(CO)₂(4-Bzpy) complex in deoxygenated dichloromethane at 293 K gives rise to an emission lifetime of 3.5 (±0.4) μs. In low-temperature (77 K) 2-MeTHF the long wavelength component of the structured emission from CpRe(CO)₂(3-Bzpy) appearing as a shoulder at 600 nm and the single emission band of CpRe(CO)₂(4-Bzpy) at 607 nm yield lifetimes of 8.6 (±0.9) and 8.7 (±0.9) μs, respectively. However, lifetime measurements from CpRe(CO)₂(3-Bzpy) in the 400–500-nm region of the 77 K spectrum reveal an except-

ionally long-lived component (>320 μs) that is beyond the time scale capability of our instrumentation. We have observed similarly long-lived emissions for the 3-Bzpy and 4-Bzpy free ligands in 2-MeTHF at 77 K; the literature emission lifetime values for these molecules in EPA glasses at 77 K have been reported to be 5.0 and 3.2 ms, respectively.[5a]

Discussion

Electronic Characteristics of 3-Bzpy and 4-Bzpy Free Ligands. The absorption spectral data obtained from the free ligands indicate that both isomers exhibit properties common to aromatic ketones.[16] In each case the two major bands observed at ~340 and ~250 nm can be assigned to spin-allowed absorptions (see Figure 1). The low molar absorptivity ($\epsilon \sim$ 100 M^{-1} cm^{-1}) for the long-wavelength feature enables it to be assigned to a n,π^* transition; this assignment is consistent with its observed hypsochromic shift as the solvent becomes more polar (see Table I).[16,17] On the other hand, the high molar absorptivity ($\epsilon \sim$ 10 000 M^{-1} cm^{-1}) of the short-wavelength band permits it to be assigned to a π,π^* transition; this assignment is supported by its observed bathochromic shift when the solution is changed to a more polar medium (see Table I).[16,17] A comparison of the energies of the π,π^* bands of the two molecules in the same solvent reveals that the π,π^* transition of the 4-Bzpy ligand is at longer wavelength. This is consistent with the more extensively conjugated system for 4-Bzpy, where there is expected to be an increased amount of delocalization between the carbonyl group and the aromatic rings in this molecule.[17c]

Further evidence for the differing electronic characteristics of 3-Bzpy and 4-Bzpy arises from the n,π^* absorptions as only the former molecule exhibits distinct vibrational structure (see Figure 1 and Table II); the observed vibrational progression ($\Delta\nu_{av}$ = 1102 cm^{-1}) for 3-Bzpy corresponds to the C=O stretch of this singlet excited state $S_1(n,\pi^*)$.[16] Apparently, the C=O group in 3-Bzpy can undergo the stretching vibrational motion rather independently, whereas the C=O moiety in 4-Bzpy is more strongly coupled with the aromatic rings.

Photophysical Properties of 3-Bzpy and 4-Bzpy Free Ligands. Several interesting conclusions can be drawn from the emission data of the free ligands obtained at room and low temperature (see Figures 4 and 5 and Table III). The 3-Bzpy molecule exhibits well-resolved structure with an average vibrational progression ($\Delta\nu_{av}$) of 1659 cm^{-1} at 293 K and 1568 cm^{-1} at 77 K; these values correspond well with the C=O stretching vibration of the ground-state molecule.[16,17a] In contrast, while the 4-Bzpy ligand also exhibits emission with a well-defined vibrational structure, the average progression ($\Delta\nu_{av}$) of 1388 cm^{-1} at 293 K and 1309 cm^{-1} at 77 K is considerably smaller and is associated with the aromatic ring C=C vibration.[17a] The results clearly indicate that in the case of 3-Bzpy emission occurs from a triplet n,π^* state following population of the corresponding singlet n,π^* level. On the other hand, in 4-Bzpy the emission apparently arises from a triplet π,π^* level after population of the singlet n,π^* state, implying that there is a crossover between the levels here. Previously, the photophysical processes of aromatic carbonyls have been studied and analogous phenomena have been reported.[18] It has been suggested that the photophysics in these types of molecules may be influenced by an intramolecular energy-transfer process between the n,π^* and π,π^* triplet levels.

These photophysical observations are concordant with the above electronic absorption results. In the case of 4-Bzpy the carbonyl

group is heavily perturbed by the neighboring aromatic rings and facile intramolecular energy-transfer mechanisms to the lowest-lying π,π^* triplet level are able to take place. Contrastingly, the carbonyl group in 3-Bzpy is relatively unperturbed by the aromatic rings and following conventional intersystem crossings the emission arises from the lowest n,π^* triplet level. Solvent effects on the emission data further support this analysis. When the nonpolar isooctane solution is replaced by a more polar dichloromethane solution the emission band of 3-Bzpy blue-shifts, while the emission band of 4-Bzpy red-shifts (see Results). These observations are in agreement with the assignments of a triplet n,π^* emission for 3-Bzpy and a triplet π,π^* emission for 4-Bzpy.

Electronic Characteristics of CpRe(CO)$_2$L Complexes. Previously, the electronic structures of the related CpFe(CO)$_2$X (X = I, Br, and Cl) complexes[19] and other CpRe(CO)$_2$L (L = CO or a N-donor ligand) complexes[8,11] have been investigated in considerable detail. Also, the 3-benzoylpyridine and 4-benzoylpyridine molecular systems have been studied as coordinated ligands in the closely related *fac*-XRe(CO)$_3$L$_2$ species.[5] Analyses of the low-binding energy region of the ionization spectra of CpM-(CO)$_3$ (M = Mn and Re)[19,20] and the photoelectron spectra (PES) of the corresponding CpM(CO)$_2$L derivatives[11] have indicated that CpM(CO)$_3$ (M = Mn and Re) can be represented as having "pseudo-O_h" symmetry with the "t_{2g}" orbitals being split by about 0.4 eV (see Figure 9). Approximate calculations on CpFe(CO)$_2$X (X = I, Br, and Cl) have demonstrated that the symmetry of these complexes may be treated in terms of a perturbation of the C_{4v}-symmetry of Mn(CO)$_5$X complexes, recognizing that the degeneracy of the eigenvalues is not substantially lost in the iron complexes on changing the central metal atom and substituting the cyclopentadienyl ring for the carbonyl ligands.[20a]

Consequently, a molecular orbital description based on these symmetry approximations for the CpRe(CO)$_3$ and CpRe(CO)$_2$L complexes is illustrated in Figure 9; this scheme also indicates the different electronic characteristics of the donor orbitals of the 3-Bzpy and 4-Bzpy ligands. In this simple MO representation the lowest-energy transitions of the parent CpRe(CO)$_3$ molecule are of ligand field (LF) character and originate between "t_{2g}" and "e_g" type orbitals. However, in the CpRe(CO)$_2$L (L = 3-Bzpy and 4-Bzpy) species the lowest-energy transitions are of metal-to-ligand charge-transfer (MLCT) character; these transitions arise from the degeneracy removal of the filled "t_{2g}" type orbitals to yield orbitals of "b_2" and "e" symmetries.[8b,11,19,20a] The lowest unoccupied molecular orbitals (LUMO) in the CpRe(CO)$_2$L system are the acceptor-π^* orbitals in the ligand itself which are virtually degenerate,[21] as their splitting energy does not increase appreciably upon coordination.[11] Furthermore, the two intraligand transitions, IL(n,π^*) and IL(π,π^*), are anticipated to occur at energies similar to those observed in the corresponding free ligands. Although this MO model is regarded as a gross approximation, it does prove useful in rationalizing the obtained absorption and photophysical data.

Our absorption spectral observations are entirely in agreement with the proposed electronic structure model. The absorption spectra of CpRe(CO)$_2$L (L = 3-Bzpy and 4-Bzpy) are each dominated by an intense feature in the visible region that also displays a low-energy shoulder (see Figures 1 and 2); the intense band is assigned to the b$_2 \rightarrow \pi^*$ MLCT transition, and the low-energy shoulder is assigned to the e $\rightarrow \pi^*$ MLCT transition in accordance with previous assignments based on the perturbed-C_{4v} symmetry approximation.[13] For convenience, the two low-lying Re(dπ) $\rightarrow$ (π^*)L transitions in these CpRe(CO)$_2$L

(16) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin-Cummings: Menlo Park, CA, 1978.

(17) (a) Becker, R. S. *Theory and Interpretation of Fluorescence and Phosphorescence*; Wiley: New York, 1969. (b) Birks, J. B. *Organic Molecular Photophysics*; Wiley: New York, 1975; p 142, Vol. 2. (c) Bartrop, J. A.; Coyle, J. D. *Excited States in Organic Chemistry*; Wiley: New York, 1975; p 29.

(18) (a) Ermolaev, U.; Terenin, A. *Soviet Phys. Usp.* **1960**, *3*, 423. (b) Lim, E.; Yu, J. *J. Chem. Phys.* **1966**, *45*, 4742.

(19) Fenske, R. F.; Dekock, R. L. *Inorg. Chem.* **1970**, *9*, 1053.

(20) (a) Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1978**, *98*, 50. (b) Orgel, L. E. *J. Inorg. Nucl. Chem.* **1956**, *2*, 315.

(21) (a) Geoffroy, G. L.; Wrighton, M. S. In *Organometallic Photochemistry*; Academic Press: New York, 1979. (b) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 3825. (c) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1986**, *25*, 3212.
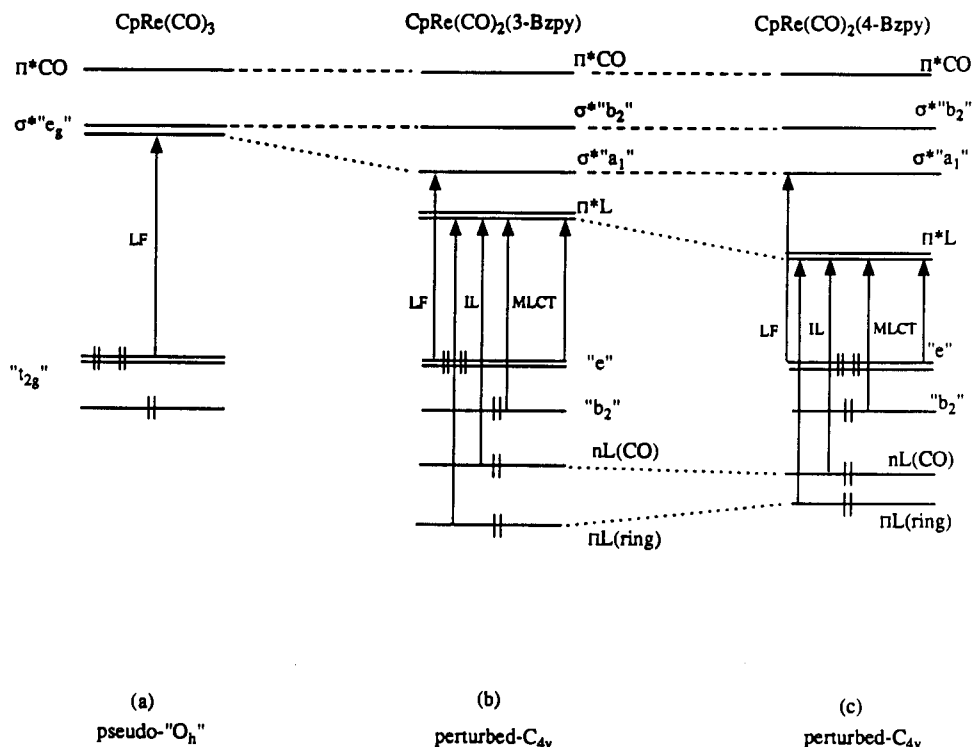
Figure 9. Molecular orbital scheme for (a) pseudo-O_h CpRe(CO)₃, (b) perturbed-C_{4v} CpRe(CO)₂(3-Bzpy), and (c) perturbed-C_{4v} CpRe(CO)₂(4-Bzpy) complexes. For clarity only the lowest-lying IL, LF, and MLCT transitions are illustrated. The designations nL(CO) refer to the carbonyl groups of the pyridino ligands.

complexes are hereafter denoted as originating from ³MLCT(b₂) and ³MLCT(e) excited states. Noticeably, both of these transitions exhibit solvent and substituent dependencies (see Figure 2 and Table I) that are characteristic of MLCT spectra from other metal carbonyl systems.[1,21] Moreover, the MLCT bands are temperature/environment sensitive, shifting to higher energy when the 2-MeTHF solution is cooled to a frozen glass (see Figure 3), consistent with the solvent changes deriving from the reorientation of the solvent dipoles around the metal complexes as the medium becomes rigid.[1,8,21,22]

The higher-energy absorption bands in the CpRe(CO)₂L complexes are assigned as singlet π,π* intraligand (¹IL) transitions localized on the molecular ring system because the energy positions, shapes, and molar extinction coefficients of these bands are almost the same as those of the corresponding free ligands (see Figure 1 and Table I). In contrast, the n,π* transitions of the free 3-Bzpy and 4-Bzpy ligands have relatively low molar extinction coefficients (see Table I) and it is, therefore, reasonably expected that the CpRe(CO)₂L (L = 3-Bzpy and 4-Bzpy) complexes also have relatively weak n,π* absorption bands. In fact, the n,π* absorption bands cannot be observed for either of the CpRe(CO)₂L complexes as the neighboring MLCT bands are intense and effectively mask them.

The lowest-lying LF transitions for the CpRe(CO)₂L species are also expected to be present in the near-UV region and, indeed, have been identified at ~340 nm for CpRe(CO)₂(pip) (pip = piperidine).[8] However, in these particular 3-Bzpy and 4-Bzpy derivatives the corresponding lowest-lying LF absorption bands are again rather obscured and overlapped by the intense neighboring IL and MLCT transitions (see Figure 1).

Photophysical Properties of CpRe(CO)₂L Complexes. As noted above, the CpRe(CO)₂(3-Bzpy) complex clearly displays two distinct emission maxima, A and B, in either room-temperature

dichloromethane or isooctane solutions (see Figure 6a and Table IV). The lowest-energy emission band B (at 610 nm in dichloromethane) is noted to be both solvent and substituent dependent and is, therefore, associated with the ³MLCT levels. The other emission feature, band A, is observed at higher energy, and this band exhibits relatively little solvent dependence. Moreover, its energy position (at 455 nm in dichloromethane solution) is very similar to that of the emission from the free 3-Bzpy ligand (see Figures 4 and 6 and Tables II and IV). Consequently, band A is assigned to the lowest-energy triplet intraligand (³IL) transition arising from the n,π* level. Although the half-width of the emission band A from CpRe(CO)₃(3-Bzpy) is also similar to the n,π* emission band of the free ligand in the same solvent, the former feature has apparently lost its vibrational structure. This is attributed to the addition of low-frequency vibrational modes when the ligand is coordinated to the Re(I) metal center. Importantly, the CpRe(CO)₂(4-Bzpy) complex exhibits only one broad emission feature centered at 625 nm (see Figure 6b). This is also solvent and substituent dependent and, consequently, is assigned to the lowest-energy ³MLCT excited states.

Emission spectra of these two CpRe(CO)₂L complexes have been shown to undergo significant changes when the solution is cooled to 77 K, and these are consistent with the MLCT assignment. The ³MLCT band of the CpRe(CO)₂(3-Bzpy) complex blue-shifts substantially when the solution is cooled to a frozen glass, and it overlaps significantly with the ³IL band (see Figure 8a). The ³MLCT band of the CpRe(CO)₂(4-Bzpy) complex also exhibits a detectable blue-shift and is intensified when the solvent becomes a rigid glass (see Figure 8b). Previously, it has been shown that MLCT emission bands are especially affected when the solution changes from fluid to a rigid matrix; this phenomenon has been termed "luminescence rigido-chromism"[5b,22a] and has been observed for a number of other substituted metal carbonyl complexes.[1,8,21,22] It is understood to arise from the changing solvent environment (and hence the dipolar interactions) surrounding the emitting complex as the medium freezes and becomes rigid. Recently, this phenomenon

(22) (a) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998. (b) Salman, O. A.; Drickamer, H. G. *J. Chem. Phys.* **1982**, *77*, 3337. (c) Rawlins, K. A.; Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1990**, *29*, 3866. (d) Kotch, T. G.; Lees, A. J.; Fuerniss, S. J.; Papathomas, K. I. *Chem. Mater.* **1992**, *4*, 675. (e) Kotch, T. G.; Lees, A. J.; Fuerniss, S. J.; Papathomas, K. I.; Snyder, R. *Inorg. Chem.* **1991**, *30*, 4871.

has been explored for a series of *fac*-XRe(CO)₃L (X = Cl, Br, I; L = α,α'-diimine) complexes during the formation of various polymeric structures.[22d,e]

Noticeably, the higher energy emission band A obtained from CpRe(CO)₂(3-Bzpy) exhibits structure when the solution is cooled to 77 K and becomes a glass. In making a comparison with the emission spectrum of the free 3-Bzpy ligand under the same conditions, it can be seen that both the vibrational progression and energy position of these ³IL (n,π*) bands are analogous, but the band structure of the organometallic complex is somewhat less well resolved (see Figures 5a and 8a). This may, as noted above, be also due to the introduction of low-frequency vibrations on the ligand emission upon coordination of the ligand at the metal center. In contrast, even in low-temperature (77 K) glasses a ³IL emission band still cannot be observed from the CpRe-(CO)₂(4-Bzpy) complex. This aspect is discussed below.

It should be recognized that while two charge-transfer bands, ³MLCT(e) and ³MLCT(b₂), were observed in the absorption spectra for each of these CpRe(CO)₂L complexes in either room-temperature or low-temperature glassy solutions, only one emission ³MLCT band has been detected under the same conditions. This impels us to believe that the excited ³MLCT(e) and ³MLCT(b₂) levels actually lie close in energy and are thermally equilibrated at both room and low temperatures. The observed MLCT emission from either complex is thus regarded to arise from a manifold of rapidly interconverting ³MLCT(e)/³MLCT(b₂) states, although it should be recognized that our data do not reveal whether the upper ³MLCT level is actually populated. Emission lifetimes obtained from the CpRe(CO)₂L complexes at 293 and 77 K (see Table IV) also support the ³IL and ³MLCT assignments. Although the values for the low-energy emission bands at room temperature are fairly long (3.5–5.2 μs), they are not unusual for ³MLCT states.[1] When the solution temperature is lowered to 77 K and the solution becomes a glass, the lifetimes become longer (~9 μs; see Table IV), consistent with a reduction in the nonradiative decay pathways from these states. The exceptionally long lifetime (>300 μs) obtained for the higher-energy emission from CpRe(CO)₂(3-Bzpy) is concordant with the triplet n,π* assignment. Significantly, the measured lifetimes for bands A and B of CpRe(CO)₂(3-Bzpy) are identical (within experimental error) over the temperature range of 278 to 298 K, suggesting that the ³IL and ³MLCT manifold states are also interconverting and are, thus, thermally equilibrated in fluid solution. At 77 K, however, the emission lifetimes obtained from each of the emission bands are different (see Table IV), indicating that the thermal equilibrium between the ³IL and ³MLCT manifold states is lost in a low-temperature frozen glass.

Finally, the excitation spectra of the complex can be understood in terms of the ³IL/³MLCT dual-luminescence model. When the emission of CpRe(CO)₂(3-Bzpy) is monitored at the wavelengths corresponding to either of the ³IL or ³MLCT emission maxima (bands A and B, respectively), the excitation spectra were noted to be essentially identical and congruent with the absorption band envelope. This is supportive of a model involving rapidly equilibrating ³IL and ³MLCT levels. The excitation spectrum of the CpRe(CO)₂(4-Bzpy) complex also provides information on the nature of the photophysical processes. When the emission is monitored at wavelengths corresponding to the ³MLCT emission maximum, the excitation spectrum exhibits a feature centered at ~390 nm that is not congruent with the MLCT absorption band envelope but rather appears to correspond to the ¹IL(n,π*) level. This result suggests that the ¹IL(n,π*) state is especially able to effectively populate the emitting ³MLCT(e)/³MLCT(b₂) manifold levels in the CpRe(CO)₂(4-Bzpy) complex. If the ¹MLCT(e) or ¹MLCT(b₂) levels are excited directly, there are clearly other deactivation processes which are strongly competitive. These may, for example, involve efficient nonradiative processes directly from the ¹MLCT(e) and ¹MLCT(b₂)

states to the ground state as has been recently found for W(CO)₅-(4-CNpy).[23] Moreover, this observation also gives us an important indication as to why the ³IL(n,π*) emission cannot be observed in the CpRe(CO)₂(4-Bzpy) complex. This point will be further discussed below.

Excited-State Dynamics. In the last ten years a number of multiple-state luminescence systems have been studied, and most cases involve multiple luminescence only at low temperature.[1,2] The CpRe(CO)₂(3-Bzpy) molecule is particularly important because a dual-luminescence spectrum is observed from the complex in fluid solution at room temperature. Only a few similar examples have been observed previously,[1,3,7,8,22c] and therefore, a study of the dynamic process that exists between the ³IL and ³MLCT excited states is significant.

Analysis of the luminescence data for CpRe(CO)₂(3-Bzpy) leads to the conclusion that the two emitting ³IL and ³MLCT states are in thermal equilibrium under room-temperature solution conditions. This is because of the following: (a) The two emission bands A and B exhibit no discernible variation when the exciting wavelength is moved throughout the broad absorption band envelope. (b) The emission lifetimes of the participating ³IL and ³MLCT states are found to be equivalent. (c) The obtained excitation spectrum of the complex is not affected by changes in the monitoring emission wavelength throughout the dual-luminescence bands. Moreover, from the data recorded just above the glass transition point, it can be inferred that the thermal equilibrium appears to exist at any temperature where the medium is still fluid. On the other hand, the results obtained from the 2-MeTHF glassy solution at 77 K illustrate that the thermal equilibrium between the ³IL and ³MLCT states is destroyed when the environment becomes rigid. This is evidenced by the luminescence spectral distribution being dependent on the wavelength of exciting light and by the fact that the emission lifetimes of the participating ³IL and ³MLCT states are not equal at 77 K.

In order to more clearly describe the dynamic processes between the ³IL and ³MLCT excited levels for CpRe(CO)₂(3-Bzpy), the emission spectral data were recorded over a range of fluid solution temperatures (see Figure 7). The results lead us to suggest that there is a Boltzmann relationship between the ³IL and ³MLCT emitting levels. In adopting a Boltzmann distribution model, we have assumed that the rate of interconversion between the ³IL and ³MLCT emitting levels is rapid compared to the rates of deactivation from these individual exciting levels.[4] Subsequently, the temperature dependence data of Figure 7 can be fitted to the modified Boltzmann expression shown in eq 1.[3,4,22c,24] Here, I_u

$$\ln(I_u/I_l) = \ln(g_u k_u/g_l k_l) - \Delta E/(k_B T) \qquad (1)$$

and I_l are the emission intensities of the upper (u) ³IL and the lower (l) ³MLCT levels measured at 454 and 610 nm, respectively, k_u and k_l represent the radiative rate constants of these states, g is a degeneracy factor, ΔE denotes the energy gap between the emitting levels, k_B is the Boltzmann constant, and T is temperature (K). A least-square analysis of the spectral results is shown in Figure 10, yielding an energy gap (ΔE) of 665 cm⁻¹ from the slope of the fitted line. This value reflects the energy difference between the 0,0 levels of the two participating excited states and is consistent with their rapid interconversion as it is well within a recognized equilibrium limit of 1000 cm⁻¹ predicted for such excited-state kinetics.[4] It also agrees well with the few other reported multiply emissive organometallic systems that are understood to be thermally equilibrated in fluid solution.[3d,8b,22c]

(23) Glyn, P.; Johnson, F. P. A.; George, M. W.; Lees, A. J.; Turner, J. J. *Inorg. Chem.* **1991**, *30*, 3543.

(24) (a) Watts, R. J.; Missimer, D. *J. Am. Chem. Soc.* **1978**, *100*, 5350. (b) Kirchoff, J. R.; McMillin, D. R.; Robinson, W. R.; Powell, D. R.; McKenzie, A. T.; Chen, S. *Inorg. Chem.* **1985**, *24*, 3928.
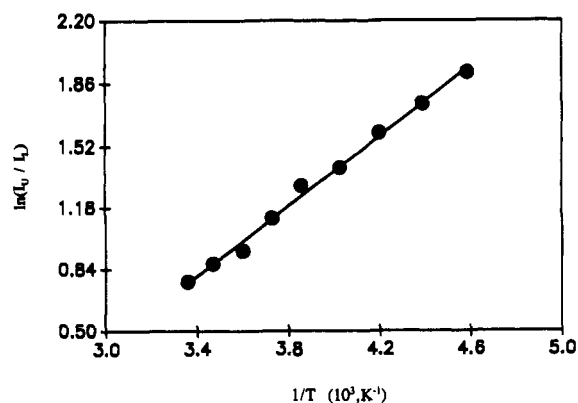
Figure 10. Plot of $\ln(I_u/I_l)$ versus $1/T$. Data are taken from Figure 7.

To understand why the CpRe(CO)₂(3-Bzpy) complex gives two emission features but the CpRe(CO)₂(4-Bzpy) complex gives only one emission feature we should first recall the different photophysical properties observed for the free 3-Bzpy and 4-Bzpy ligands. The 4-Bzpy ligand exhibited π,π^* emission character because of the increased amount of delocalization between the carbonyl group and the adjacent aromatic rings, but contrasting, the 3-Bzpy ligand exhibits a typical, n,π^* emission feature because the carbonyl group is relatively isolated. Consequently, in CpRe(CO)₂(4-Bzpy), the Re(dπ^*), L(π), and L(π^*) orbitals can readily mix but in CpRe(CO)₂(3-Bzpy) the L(n) orbital (localized on the ketone oxygen) is relatively isolated and may not mix with these other levels. The key point is that the n,π^* state need only be perturbed to the extent that the L(π^*) orbital interacts with

the Re(dπ) levels. Therefore, the ³IL(n,π^*) and ³MLCT(dπ,π^*) excited states in CpRe(CO)₂(3-Bzpy) are likely to have substantially differing geometries. In contrast, internal conversion between the ³IL(π,π^*) and ³MLCT(dπ,π^*) states in the CpRe(CO)₂(4-Bzpy) complex is likely to be facilitated by the mixing of the states and possibly by geometrical similarities. Furthermore, the larger energy gap that exists between the ³IL and ³MLCT states in the latter complex could also explain why only a single emission is observed.

Conclusion

The observed spectroscopic results have enabled us to describe the photophysical deactivation mechanisms of CpRe(CO)₂-(3-Bzpy) and CpRe(CO)₂(4-Bzpy) complexes in fluid solution and in rigid glassy conditions. The photophysical properties of the two complexes are strikingly different: CpRe(CO)₂(3-Bzpy) has been found to be a multiple-state emitter, whereas CpRe-(CO)₂(4-Bzpy) exhibits emission from a single state. This behavior is rationalized in terms of the different electronic characteristics of the ligands and the excited-state kinetics of these CpRe(CO)₂L complexes. The multiple-state emission is detectable even at room temperature, and it is shown to conform to a modified Boltzmann model.