Photophysical Effects of Metal–Carbon σ Bonds in Ortho-Metalated Complexes of Ir(III) and Rh(III)

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Abstract: Dichloro-bridged dimers of the type [M(L)$_2$Cl]$_2$, where L is 2-phenylpyridine (ppy) or benzo[*h*]quinoline (bzq) and M is Rh(III) or Ir(III), have been characterized by ^{13}C and ^{1}H NMR spectroscopies and by absorption and emission spectroscopies. The NMR results confirm previous formulations of the complexes as dichloro-bridged ortho-metalated dimers in halocarbon solvents but indicate that they are cleaved to monomeric species of the type M(L)$_2$ClS in ligating solvents such as dimethylformamide (S = solvent). The absorption spectra of each of the complexes contain several low-energy bands which are assigned as metal-to-ligand charge-transfer (MLCT) transitions. All four of the dimers emit light following photoexcitation of their glassy solutions at 77 K. Their emission spectra and lifetimes lead to assignments of their emitting states as intraligand (π–π*) for the Rh(III) dimers and MLCT (d–π*) for the Ir(III) dimers. The Ir(III) dimers are also found to emit light following excitation at 295 K in deaerated dichloromethane. No emission is seen from the Rh(III) dimers under these conditions. Comparison of these results with previous results from studies of similar Rh(III) and Ir(III) complexes of 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) indicates that the ortho-metalated ligands are considerably higher than bpy and phen in the spectrochemical series. In addition to raising the energy of ligand field excited states in their complexes, relative to similar bpy and phen species, they induce lower energy charge-transfer transitions. These effects are consistent with the synergistic function of the ortho-metalated ligands as both strong σ donors and π acceptors.

I. Introduction

Recent studies of the reaction of 2,2′-bipyridine (bpy) with Ir(III)[1-7] indicate that metalation sometimes occurs at the C-3 position of a pyridine ring adjacent to a second, N-coordinated pyridine ring in bpy. A similar result has been reported[8] in the reaction of *N*-methyl-2,2′-bipyridinium ion (mebpy) with Pt(II). The former reaction was unanticipated since bpy generally coordinates through the N atom of each of the two pyridine rings (N,N′ isomer). The process is an unusual example of a broad class of orthometalation reactions[9,10] and leads to the C³,N′ isomer of one of the three coordinated bpys.
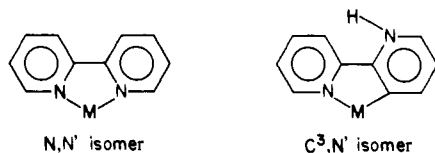
Orthometalation reactions are common in ligands which contain a benzene ring attached to a functional group containing a donor atom. Ligands of this type include several which are structurally similar to bpy, such as 2-phenylpyridine (ppy) and benzo[*h*]-quinoline (bzq).
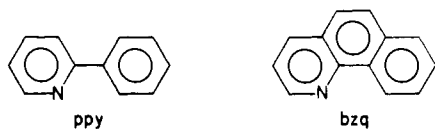
Ortho-metalated complexes of these ligands have been reported for a variety of transition metals, including Pd(II),[11] Pt(II),[12]

Rh(III),[13] Ir(III),[14] Os(II),[15] and Ru(II).[16,17] The mode of ligation of ppy and bzq is analogous to that found in C³,N′-bpy, and the former ligands are noted for their tendency to form binuclear dihalo-bridged metal complexes. Dihalo-bridged Ru(II) complexes of N,N′-bpy have also been prepared and studied,[18] but formation of mononuclear species such as *cis*-Ru(bpy)$_2$Cl$_2$ is far more common in the chemistry of N,N′-bpy; no bridged dimers containing C³,N′-bpy have been reported.

Although the photochemistry of transition-metal–bpy complexes has been studied extensively,[19,20] particularly with regard to their photoredox properties,[21,22] relatively little is known of the photochemical, spectroscopic, and electrochemical properties of metal complexes of the structurally similar ppy and bzq ligands.[23] In fact, the extensive literature on organometallic photochemistry includes very little characterization of the photochemical properties of metal–carbon σ bonds to aromatic π-conjugated ligands. Well-studied ligands such as CO and CN, which form metal–carbon bonds readily, are known to lie at the top of the spectrochemical series. Although these ligands are noted for their strong metal–ligand π-back-bonding abilities, they lack the extended ligand-based π-conjugation of bpy-like ligands, and, therefore, their complexes do not generally display the low-energy MLCT states which are characteristic of many of the metal–bpy complexes. Hence, upward movement of the ligand field (LF) state energies induced by formation of metal–carbon bonds, analogous to CO and CN, as well as low-energy MLCT bands, analogous to metal–bpy complexes, are anticipated in complexes of ppy and bzq. This anticipated upward movement of LF states coupled with low-energy MLCT states might alter significantly the spectroscopic and electrochemical patterns established[24-27] for structurally similar

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metal–bpy or 1,10-phenanthroline (phen) complexes. Furthermore, the established tendency of these ligands to form binuclear species is indicative of the distinct thermal reactivity patterns which they impart to their metal complexes through modification of the electron density in the metal coordination sphere. This is expected to lead to photoreactivity patterns which are similarly distinct from those characteristic of metal–bpy complexes. In addition, some modifications of photochemical and spectroscopic properties might result from potential interactions of the two metal centers, either through direct metal–metal bonding or through the bridging chloride ligands.

In view of the potential impact of metal–carbon bond formation on the excited-state properties of metal complexes of these ligands, and of the well-established role of metal–carbon bonds in areas such as organic synthesis and catalysis, we have undertaken a study of the thermal and photochemical properties of ppy and bzq complexes. Reported here are results of a study of the dichloro-bridged dimeric complexes of ppy and bzq with Ir(III) and Rh(III).

II. Experimental Section

A. Syntheses. Tetrakis(2-phenylpyridine-C^2,N')(μ-dichloro)dirhodium.[13] Rhodium trichloride trihydrate (0.500 g, Alfa-Ventron) was mixed with 2-phenylpyridine (4.0 mL, Aldrich) and dissolved in glycerol (10 mL). The solution was heated at 150 °C for 22 h and cooled to room temperature. HCl (30 mL, 1.0 M) was added, and the reaction mixture was refrigerated for 3 h. The precipitate was collected on a glass filter frit and washed with HCl (100 mL, 1.0 M), methanol (60 mL), and dichloromethane (4 mL). The remaining precipitate was dissolved in dichloromethane (60 mL) and filtered. The filtrate was evaporated, and the yellow product was collected to yield [Rh(ppy)$_2$Cl]$_2$·$^1/_4$CH$_2$Cl$_2$ (0.692 g, 81.7%).

Anal. Calcd for Rh$_2$C$_{44}$H$_{32}$N$_4$Cl$_2$·$^1/_2$CH$_2$Cl$_2$: C, 58.0; H, 3.7; N, 6.1; Cl, 9.7. Found: C, 58.3; H, 3.6; N, 6.0; Cl, 8.6.

Molecular weight in dichloroethane: calcd 893 g/mol, found 795 g/mol.

Tetrakis(benzo[*h*]quinoline-C^{10},N')(μ-dichloro)dirhodium.[13] Rhodium trichloride trihydrate (0.500 g, Alfa-Ventron) was mixed with benzo-[*h*]quinoline (0.850 g, Fluka) and dissolved in glycerol (8 mL). The solution was heated at 170 °C for 24 h and then cooled to room temperature. HCl (30 mL, 1.0 M) was added, and the reaction mixture was refrigerated overnight. The precipitate was collected on a glass filter frit and washed with HCl (150 mL, 1.0 M) and methanol (40 mL). This precipitate was then dissolved in three portions of dichloromethane (10, 20, and 60 mL). Hexanes (30 mL) were added to each of the first two portions, and the resulting precipitates were collected. The 60-mL portion was evaporated to dryness, and the solid product was combined with the dried precipitates from the first two portions to yield [Rh(bzq)$_2$Cl]$_2$ (0.902 g, 96.0%).

Anal. Calcd for Rh$_2$C$_{52}$H$_{32}$N$_4$Cl$_2$: C, 63.1; H, 3.3; N, 5.7; Cl, 7.2. Found: C, 62.0; H, 3.5; N, 5.3; Cl, 6.4.

Molecular weight in dichloroethane: calcd 989 g/mol, found 775 g/mol.

Tetrakis(2-phenylpyridine-C^2,N')(μ-dichloro)diiridium. Iridium trichloride hydrate (0.388 g, Mathey-Bishop) was combined with 2-phenylpyridine (0.76 g, Aldrich, distilled), dissolved in a mixture of 2-ethoxyethanol (30 mL, distilled and dried over MgSO$_4$) and water (10 mL), and refluxed for 24 h. The solution was cooled to room temperature, and the yellow precipitate was collected on a glass filter frit. The precipitate was washed with 95% ethanol (60 mL) and acetone (60 mL) and then dissolved in dichloromethane (75 mL) and filtered. Toluene (25 mL) and hexanes (10 mL) were added to the filtrate, which was then reduced in volume by evaporation to 50 mL, and cooled to give crystals of [Ir(ppy)$_2$Cl]$_2$ (0.428 g, 72%).

Anal. Calcd for Ir$_2$C$_{44}$H$_{32}$N$_4$Cl$_2$: C, 49.29; H, 3.00; N, 5.23; Cl, 6.66. Found: C, 48.62; H, 2.54; N, 5.22; Cl, 4.25.

Molecular weight in chloroform: calcd 1072 g/mol, found 1023 g/mol.

Tetrakis(benzo[*h*]quinoline-C^{10},N)(μ-dichloro)diiridium.[14] Iridium trichloride hydrate (0.500 g, Mathey-Bishop) was combined with ben-

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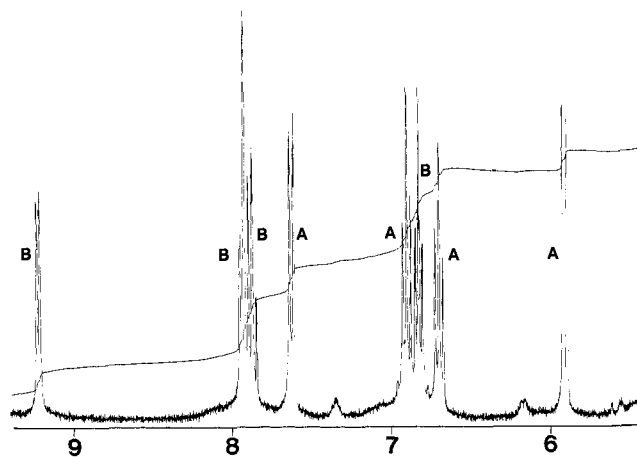
Figure 1. ^{1}H NMR spectrum of tetrakis(2-phenylpyridine-C^2,N')(μ-dichloro)dirhodium in dichloromethane-d_2.
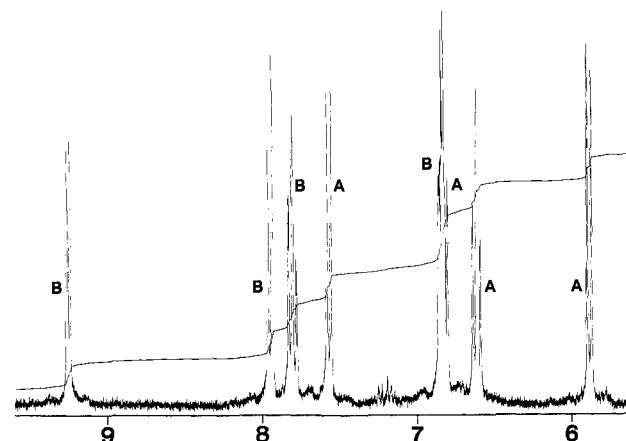

Figure 2. ^{1}H NMR spectrum of tetrakis(2-phenylpyridine-C^2,N')(μ-dichloro)diiridium in dichloromethane-d_2.

zo[*h*]quinoline (1.240 g, Fluka, sublimed), and the reaction and isolation of the product was carried out analogously to that for the 2-phenylpyridine complex to give [Ir(bzq)$_2$Cl]$_2$·C$_7$H$_8$ (0.400 g, 40%).

Anal. Calcd for Ir$_2$C$_{52}$H$_{32}$N$_4$Cl$_2$·C$_7$H$_8$: C, 56.22; H, 3.20; N, 4.44. Found: C, 56.14; H, 3.57; N, 3.85.

Molecular weight determined in dichloroethane: calcd 1168 g/mol, found 1189 g/mol.

B. Measurements. ^{1}H and ^{13}C NMR spectra were obtained on a Nicolet NT-300 FT NMR spectrometer. Samples were generally dissolved in dichloromethane-d_2 for analyses. A few samples were studied in dimethylformamide-d_7 to check for dissociation of the dimers. Single-frequency off-resonance decoupled (SFORD) ^{13}C spectra were obtained for purposes of assigning nonprotonated carbons. Low-temperature (77 K) and room-temperature emission spectra were obtained with a Perkin-Elmer MPF-3 spectrophotofluorimeter. Luminescence lifetimes were determined with 336-nm pulses from an Avco C950 nitrogen laser or with third harmonic pulses (354 nm) from a Quanta Ray DCR-1 Nd/YAG laser. The optics, detection, and analyses techniques used in these measurements have been described in previous publications.[28,29] Absorption spectra were determined with a Cary 15 spectrophotometer. The low-resolution mass spectrum was measured for [Rh(ppy)$_2$Cl]$_2$ on a ZAB 2F double-focusing reverse-geometry mass spectrometer employing positive ionization at 200 °C and 5 × 10^{-5} torr.

III. Results

A. ^{1}H and ^{13}C NMR Spectra. Previous descriptions of the reactions of Rh(III) with ppy and bzq[14] and of Ir(III) with bzq[15] indicate that the dihalo-bridged dimers [Rh(ppy)$_2$Cl]$_2$, [Rh(bzq)$_2$Cl]$_2$, and [Ir(bzq)$_2$Cl]$_2$ are formed. Present results indicate that the previously unreported reaction of Ir(III) with ppy yields the analogous [Ir(ppy)$_2$Cl]$_2$ dimer.

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Table I. ^{13}C NMR Data for 2-Phenylpyridine (ppy), Benzo[*h*]quinoline (bzq), and Their Dichloro-Bridged Dimeric Complexes with Rh(III) and Ir(III) in Dichloromethane-d_2
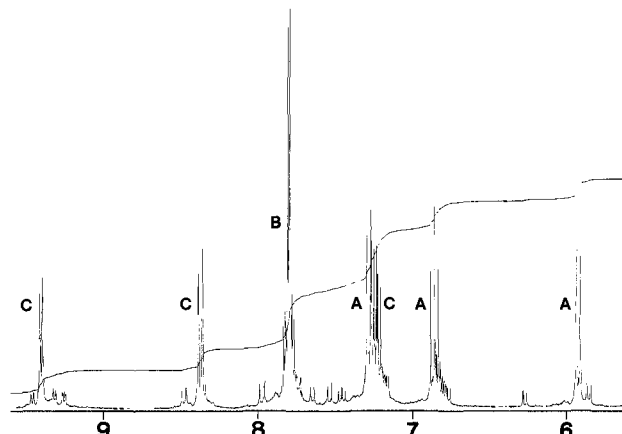
	^{13}C NMR resonances, δ											
ppy	157.4[a]	150.0[b]	139.7[a]	136.9	129.2	129.0	127.1	122.4	120.5			
[Ir(ppy)₂Cl]₂	168.0[a]	151.5[b]	144.8[a]	144.0[a]	136.6	130.3	129.0	123.6	122.5	121.4	118.7	
[Rh(ppy)₂Cl]₂	166.2, 165.8[a,c]	165.0[a]	152.1[b]	143.8[a]	136.7	131.9	128.9	123.5	122.4	122.3	118.8	
bzq[d]	149.3[b]	146.8[a]	136.1[b]	134.0[a]	132.0[a]	128.5	128.1	127.9	127.3	126.8[a]	125.8	124.6	122.2
[Ir(bzq)₂Cl]₂	158.2[a,e]	151.1[b]	141.7[a]	141.3[a,e]	136.2	133.9[a]	129.6	128.9	127.9	127.1[a]	124.0	122.1	119.7
[Rh(bzq)₂Cl]₂	163.0, 162.6[a,f]	155.4[a]	151.5[b]	140.3[a]	135.8	133.7[a]	129.7	129.4	128.7	127.3[a]	123.9	122.3	120.7

[a] Resonance shows no strong coupling to ^{1}H in SFORD. [b] Line width greater than that of other resonances; sidebands present. [c] Rh–C coupling constant = 37.8 Hz. [d] Spectrum measured in dimethyl-d_6 sulfoxide due to improved resolution in this solvent. [e] Weak signal: difficult to observe in SFORD. [f] Rh–C coupling constant = 36.7 Hz.
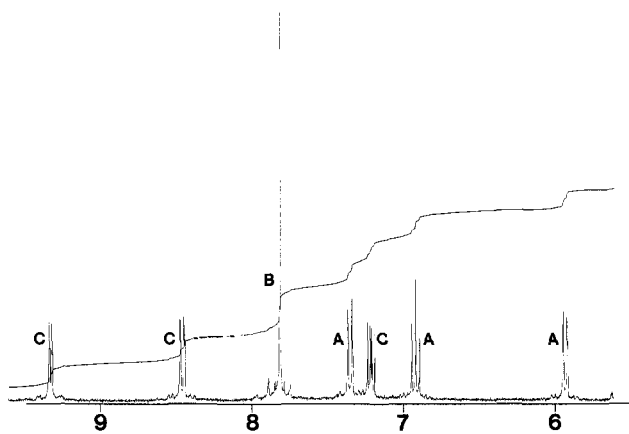
Figure 3. ^{1}H NMR spectrum of tetrakis(benzo[*h*]quinoline-C^{10},N')(μ-dichloro)dirhodium in dichloromethane-d_2.

Figure 4. ^{1}H NMR spectrum of tetrakis(benzo[*h*]quinoline-C^{10},N')(μ-dichloro)diiridium in dichloromethane-d_2.

Proton NMR data for the ppy and bzq complexes of Rh(III) and Ir(III) in dichloromethane-d_2 are illustrated in Figures 1–4. Whereas the uncomplexed ppy ligand shows a set of poorly resolved multiplets with chemical shifts ranging from δ 7.28 to 8.65 which integrate for nine protons, the two metal–ppy complexes show eight well-resolved multiplets. These lie in the range δ 5.9–9.3 for the Rh(III) complex and in the range δ 5.8–9.3 for the Ir(III) complex. In each case the splittings of the multiplets and homonuclear decoupling data are consistent with two sets of four coupled spins as anticipated for a pyridine ring and for a metalated phenyl ring. These two rings, which are labeled A and B in Figures 1 and 2, can be identified on the basis of the high-field resonances in the region between δ 6.8 and 5.9. In both complexes, a doublet at about δ 5.9 and a "triplet" at about δ 6.7 are assigned to the two protons of the phenyl ring ortho and meta to the metalated carbon atom, respectively. These assignments are consistent with previous assignments of high-field resonances in ortho-metalated bpy complexes:[6–8] protons ortho and meta to the metalated C atom experience the largest shielding of any of the ligand protons.

The proton NMR spectra of the bzq complexes in dichloromethane-d_2 have some similarities to those of the ppy complexes. However, due to more extensive coupling in the fused-ring systems, assignments are more difficult. The Rh(III) complex of bzq features seven chemical shifts in the range δ 5.9–9.4. As the sharp singlet at δ 7.9 integrates for two protons while the other multiplets integrate for one proton each, the spectrum indicates the presence of eight protons. Proton chemical shifts of the Ir complex of bzq also appear in the range δ 5.9–9.4. Integration using high- and low-field multiplets as standards for one proton clearly shows eight protons. Homonuclear decoupling results on both the Rh and Ir complex indicate the presence of three rings with coupled groups of three, two, and three spins, which are labeled A, B, and C in Figures 3 and 4. In each case the unique B ring can be assigned to the bridging ring of bzq which has only two bonded proton spins. As was the case for the ppy complexes, the A ring can be identified on the basis of the two high-field resonances, now at about δ 5.9 and 6.9 which are assigned to the two phenyl ring protons ortho and meta to the metalated C atom of bzq. The assignments are in agreement with previous ones[13] for these two complexes.

The ^{13}C NMR spectra of bzq and ppy and of their Rh(III) and Ir(III) complexes are compiled in Table I. Nine distinct resonances are observed in the spectrum of the uncomplexed ppy ligand, indicating symmetric equivalence of the phenyl ring carbon atoms ortho and para to the bridge bond due to rotation about the bridge. The two especially weak resonances at δ 157 and 140 are assigned to the two bridging carbon atoms which experience no nuclear Overhauser enhancement. When the ligand coordinates to Rh(III) or Ir(III), rotation about the bridge bond is no longer possible. As a result, the Ir complex of ppy shows 11 resonances in its ^{13}C NMR spectrum. A similar spectrum is observed for the Rh complex of ppy, with the exception of an additional splitting of the lowest field resonance due to coupling of ^{13}C to [103]Rh ($J_{Rh–C}$ = 37 Hz). SFORD techniques indicate that in each complex three carbon atoms are not protonated. Resonances at δ 166.0 in the Rh complex and at δ 144.0 in the Ir complex are assigned to the metalated carbon atoms in the phenyl rings of the respective species. The latter resonance is in close proximity to our previous report[6] of the Ir–[13]C resonance in [Ir(H(bpy)–C^3,N')(bpy)-N,-N')₂]³⁺ at δ 139.5, while the former resonance and [13]C–[103]Rh coupling constant are similar to those reported for other Rh(III) complexes containing metalated phenyl rings.[30,31]

Due to their limited solubilities and increased number of carbon atoms, the ^{13}C NMR spectra of the bzq complexes of Ir(III) and Rh(III) are more difficult to interpret. The ^{13}C NMR spectrum of the uncomplexed bzq ligand contains 13 lines, 4 of which are of very low intensity. SFORD techniques confirm that these four resonances arise from the four nonprotonated bridge atoms. The ^{13}C NMR spectra of the two metal complexes also display 13 chemical shifts, and, in the Rh complex, the lowest field signal is split by coupling of the metalated carbon to [103]Rh ($J_{Rh–C}$ = 37 Hz). SFORD techniques indicate the presence of five nonprotonated C atoms in each of the complexes, and the resonances at δ 162.8 in the Rh complex and at δ 141.3 in the Ir complex are assigned to the metalated C atoms.

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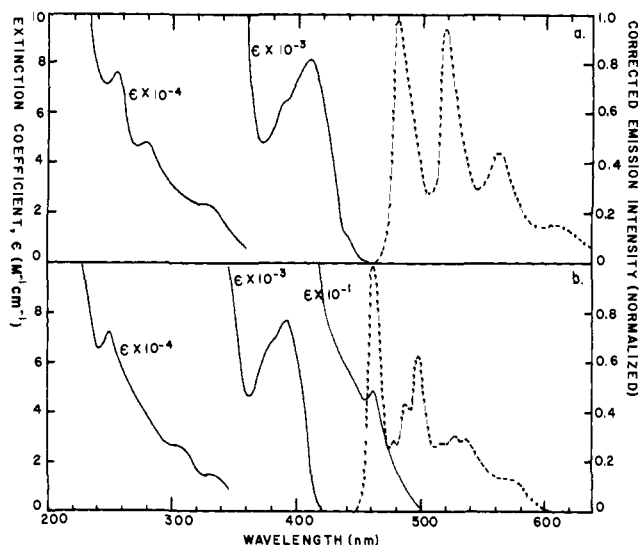
Figure 5. Absorption (—) and emission (- - -) spectra of Rh(III) dichloro-bridged dimers of 2-phenylpyridine (ppy) and benzo[h]quinoline (bzq). Absorption measured at 295 K in dichloromethane and emission at 77 K in ethanol/methanol/dichloromethane glass (4:1:1 by volume). (a) [Rh(bzq)$_2$Cl]$_2$, (b) [Rh(ppy)$_2$Cl]$_2$.
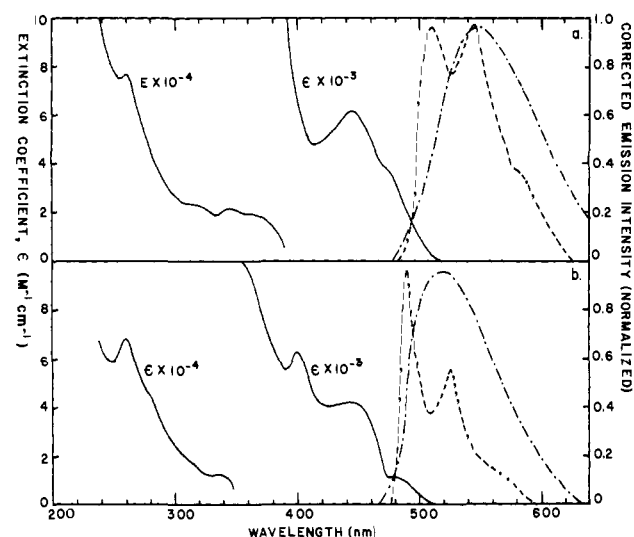

Figure 6. Absorption (—) and emission (- - -) spectra of Ir(III) dichloro-bridged dimers of 2-phenylpyridine (ppy) and benzo[h]quinoline (bzq). Absorption measured at 295 K in dichloromethane and emission at 77 K in ethanol/methanol/dichloromethane glass (4:1:1 by volume). (a) [Ir(bzq)$_2$Cl]$_2$, (b) [Ir(ppy)$_2$Cl]$_2$.

B. Absorption and Emission Properties. The absorption spectra of [Rh(bzq)$_2$Cl]$_2$ and [Rh(ppy)$_2$Cl]$_2$ in dichloromethane are shown in Figure 5, and those of [Ir(bzq)$_2$Cl]$_2$ and [Ir(ppy)$_2$Cl]$_2$ are shown in Figure 6. A complete compilation of the wavelengths and extinction coefficients for the major absorption features is presented in Table II. Measurements of the absorbance of each complex as a function of concentration in dichloromethane at the wavelengths of the major absorption features indicate that Beer's law is followed in each instance. The concentration range employed for the Rh(III) complexes was 10^{-3}–10^{-5} M, and similar results for the Ir(III) complexes were obtained over the concentration range 10^{-4}–10^{-6} M.

In contrast to the results obtained by using dichloromethane as a solvent, absorption measurements in dimethylformamide were found to deviate markedly from Beer's law. Furthermore, absorption features were found to change for several days following preparation of dimethylformamide solutions of each of the complexes. Changes in the absorption spectra of dimethylformamide solutions were dependent upon their initial concentrations. Very small changes were observed at concentrations of 10^{-3} M whereas

Table II. Absorption Data for Rh(III) and Ir(III) Dichloro-Bridged Dimers of ppy and bzq in Dichloromethane and Chloroform

complex	absorption features, nm		$10^3 \epsilon$,[a]
	CHCl$_3$ solvent	CH$_2$Cl$_2$ solvent	M^{-1} cm^{-1}
[Ir(ppy)$_2$Cl]$_2$	487 (sh)	484 (sh)	1.1
	436	434	4.2
	405	400	6.3
	355 (sh)	355 (sh)	11.0
	355	335	13.0
	260	260	68.0
[Ir(bzq)$_2$Cl]$_2$	480 (sh)	480 (sh)	3.1
	448	442	5.5
	365	363 (sh)	18.0
	349	347	20.0
	325	322 (sh)	21.0
	260	260	77.0
[Rh(ppy)$_2$Cl]$_2$	464	462	0.048
	397	393	7.7
	385 (sh)	380 (sh)	6.8
	335 (sh)	333 (sh)	15.0
	307	310 (sh)	26.0
	b	240	73.0
[Rh(bzq)$_2$Cl]$_2$	c	440 (sh)	1.1
	415	410	8.2
	400	390 (sh)	6.5
	333	330 (sh)	23.0
	280 (sh)	277	48.0
	255 (sh)	255	76.0

[a] Extinction coefficient determined in CH$_2$Cl$_2$ solvent. [b] No absorption features observed due to solvent cutoff. [c] Low-energy shoulder not observed in this solvent.

Table III. Luminescence Lifetimes of Dichloro-Bridged Rh(III) and Ir(III) Dimers of 2-Phenylpyridine (ppy) and Benzo[h]quinoline (bzq)

species	luminescence lifetime	
	77 K[a]	295 K[b]
[Rh(bzq)$_2$Cl]$_2$	2.7 ms	c
[Rh(ppy)$_2$Cl]$_2$	93.0 μs	c
[Ir(bzq)$_2$Cl]$_2$	30.0 μs	1.4 μs
[Ir(ppy)$_2$Cl]$_2$	4.8 μs	0.14 μs

[a] Measured in ethanol/methanol/dichloromethane glass, 4:1:1 by volume. [b] Measured in nitrogen-purged dichloromethane. [c] No luminescence observed in nitrogen-purged dichloromethane.

large spectral shifts were apparent when 10^{-5} M solutions were aged for several days. In the more dilute solutions the low-energy absorption features were found to be replaced by higher energy absorption bands with aging. ^{1}H NMR spectra of the Rh(III) complexes in dimethylformamide-d_7 were found to be far more complex than those measured in dichloromethane. In general, the NMR spectra indicated the presence of two nonequivalent ligands in the dimethylformamide-d_7 solvated complexes at room temperature. This was found to be the case even for solutions with concentrations as high as 10^{-2} M.

Each of the four dimers was found to be strongly luminescent in ethanol/methanol/dichloromethane (4:1:1 by volume) glasses at 77 K (see Figures 5 and 6). Luminescence spectra were also measured for nitrogen-flushed ambient-temperature dichloromethane solutions of the two Ir(III) complexes, but no emission was observed from the two Rh(III) dimers under these conditions. The emissions of the two Ir(III) complexes were very sensitive to quenching by oxygen under these conditions. Luminescence lifetimes for each of the complexes at 77 K as well as the ambient-temperature lifetimes of the Ir complexes are reported in Table III. Lifetimes of the Rh dimers were consistently longer than those of the Ir dimers, and in each case the bzq dimers were longer lived than were the ppy dimers.

IV. Discussion

A. Structural Considerations. The ^{1}H and ^{13}C NMR results reported above are consistent with the loss of a proton from ppy

and bzq in their reactions with $IrCl_3$ and $RhCl_3$ to form metalated dimers of the form $[ML_2X]_2$. In all cases the reactions occur under relatively mild conditions to yield the primary products; however, the reactions with $RhCl_3$ give higher yields of the dimer than do the $IrCl_3$ reactions. This appears to be due to the tendency of Ir(III) to form mononuclear products, several of which are presently being characterized. Initial descriptions[13] of the reactions of ppy and bzq with $RhCl_3$ indicate that metalation occurs readily under even milder conditions (refluxing ethanol) than employed in the present study. The propensity of these metal–ligand combinations to metalate under such relatively mild conditions compared to those used in preparation of metalated bpy complexes (refluxing glycerol) suggests that metalation of a phenyl ring in ppy occurs more readily than does metalation of a pyridine ring in bpy. The result does not appear to derive from competition of Ir–N bonding with Ir–C bonding in the bpy case since little of the fully N-coordinated $Ir(bpy)_3^{3+}$ is formed. Hence, the result appears to indicate reduced reactivity of a pyridine ring of bpy toward metalation in comparison to the phenyl ring of ppy. This would suggest that metalation in the ppy and bzq complexes can be viewed as an electrophilic attack[9] of the metal on an aromatic phenyl ring; relative deactivation toward metalation would then occur in bpy due to the presence of an electron-withdrawing N atom in each of the pyridine rings.

Elemental analysis of each of the complexes is consistent with the previous formulation of their structures as dichloro-bridged dimers in the solid state. This formulation is also consistent with the current mass spectroscopic results. Fragmentation of the $[Rh(ppy)_2Cl]_2$ dimer by chemical oxidation in the mass spectrometer to form $Rh(bpy)_2Cl^+$ fragments should yield several peaks in the range 446–449 amu, consistent with the mass spectrum observed for this species. An additional peak at 411 amu is believed to arise from a $Rh(ppy)_2^+$ fragment. No signals were observed in attempts to monitor the mass spectra of the Ir(III) dimers. Molecular weight determinations for each of the complexes in halocarbon solvents suggest that the dimers remain intact in these weakly coordinating solvents. Although the molecular weight determinations for the two Rh(III) complexes gave molecular weights below the anticipated values, they are clearly higher than the values which would be appropriate for monomeric species formed by cleavage of the dimers. While this might indicate an equilibrium mixture of both monomeric and dimeric species, NMR results in halocarbon solvents give no indication of the presence of nonsymmetric monomers (see below).

Both ^1H and ^{13}C NMR results clearly indicate the presence of only one type of ppy or bzq ligand in the complexes in dichloromethane. There are several structural interpretations consistent with this information. Since the M–Cl bridge bonds are known to be readily cleaved by phosphine ligands,[13,14] and the present ^1H NMR results indicate that $[Rh(ppy)_2Cl]_2$ is cleaved in a ligating solvent such as dimethylformamide (see below), a fluxional solution structure may be considered along with several symmetric static structures. A symmetric monomer of the type $M(L)_2S_2^+$, while consistent with the NMR results, is unlikely due to the weak coordinating ability of dichloromethane. Even in the presence of strongly coordinating ligands such as triphenylphosphine, the dimers cleave to yield only the monosubstituted, nonsymmetric $M(L)_2Cl(PPh_3)$ species.[13,14] Hence, cleavage of the dimer to yield the disubstituted monomer is unlikely in halocarbon solvents. The ^{13}C NMR of $[Rh(bzq)_2Cl]_2$ in dichloromethane-d_2 consists of only 13 resonances at the lowest temperature which could be studied (–40 °C) and shows no temperature dependence when the temperature is raised to 20 °C. While this cannot totally discount a fluxional structure in dichloromethane, it does render this alternative unlikely and suggests a symmetric, nonfluxional, dimeric structure. Several such structures are possible, and these may be divided into those which contain bridge bonds trans to M–C bonds and those which contain M–C bonds trans to each other. Although only a few X-ray crystal structures of similar species have been reported,[32–34] these suggest

that the M–C bond exerts a significant trans effect which favors formation of the bridge bonds trans to the M–C bonds. On these grounds, the enantiomeric pair and the meso form illustrated here are favored.
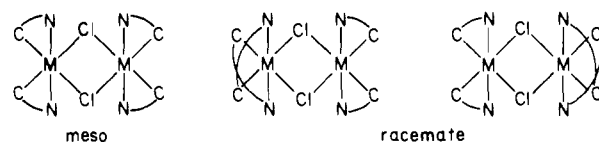
meso   racemate

Structural models suggest that interligand steric interactions in the meso form favor formation of the racemate.

B. Absorption Assignments. In discussing the excited states of ppy and bzq complexes, it is informative to draw comparisons with complexes of the structurally similar bpy and phen ligands. Although some difficulty may be encountered in this approach due to the high degree of covalency anticipated for M–C bonds, the ligand field approach, which is so convenient for well-studied bpy and phen complexes, may yield useful insights into excited-state descriptions of these complexes also. Modifications of the ligand field model to take into account the effects of bridging ligands in binuclear species have been discussed,[18,35] as have modifications to account for the high degree of covalency of M–C bonds.[36] Since the NMR and molecular weight analyses indicate that each of these complexes exists as a dimer in halocarbon solutions, the spectral analyses will be concerned primarily with results in dichloromethane.

$[Rh(bzq)_2Cl]_2$ and $[Ir(bzq)_2Cl]_2$. The unmetalated bzq ligand displays intense absorption bands at wavelengths of 270 nm ($2.5 \times 10^4 M^{-1} cm^{-1}$) and 220 nm ($4 \times 10^4 M^{-1} cm^{-1}$) as well as several weaker bands ($5 \times 10^3 M^{-1} cm^{-1}$) in the region between 300 and 380 nm. Approximate additivity of extinction coefficients for four intraligand transitions in the dimers would suggest extinction coefficients of $10^5 M^{-1} cm^{-1}$ in the region around 270 nm and $2 \times 10^4 M^{-1} cm^{-1}$ between 300 and 380 nm. These values are in rough agreement with those observed for the absorption bands in the dimers at 255–260 and 320–365 nm. Solvent shifts in the positions of the latter bands are observed, suggesting that some mixing of MLCT character with the interligand transitions occurs in this region. The absorption feature at 277 nm in the Rh complex, which is not resolved in the Ir complex, does not appear to correspond to any transition observed in the unmetalated ligand. The position of this band is red shifted in $CHCl_3$, suggesting that it may arise from a MLCT transition. However, its large extinction coefficient suggests that it may arise from special effects associated with metal–metal interactions through the dichloro bridge or with the high covalency associated with the formation of Rh–C bonds. Previous studies[18] of interactions through a dichloro bridge in $[Ru(bpy)_2Cl]_2^{2+}$ indicate that such interactions are quite small, and similarly small interactions are anticipated for these d^6 complexes of Rh(III) and Ir(III). This conclusion is confirmed by observations[37] of absorption and emission spectra of the monomeric species formed by cleavage of the dichloro bridge. The similarities of the absorption and emission spectra of these mononuclear species with the dimers are a good indication of the small degree of metal–metal interaction which occurs in the dimers. This suggests that the 277-nm absorption may best be interpreted as a consequence of the strong interactions between Rh(III) and C σ orbitals which result from bond formation. For example, a σ–σ* transition of the Rh–C bond could presumably account for bands of this type.[36]

Although the unmetalated bzq ligand has no absorption features at wavelengths greater than 380 nm, the Rh(III) and Ir(III) dimers both display several transitions in this region. A well-

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resolved band of [Rh(bzq)$_2$Cl]$_2$ at 410 nm in dichloromethane red shifts in chloroform, consistent with a MLCT assignment. A similar feature occurs in [Ir(bzq)$_2$Cl]$_2$ at longer wavelengths (442 nm) and shows a similar solvent dependence; this is also assigned as an MLCT band. Both complexes show poorly resolved shoulders at longer wavelengths. Due to the close proximity of these to the emission spectra, they may represent direct transitions to the emissive states as discussed in more detail below.

[Rh(ppy)$_2$Cl]$_2$ and [Ir(ppy)$_2$Cl]$_2$. Only two bands are observed in the ultraviolet–visible absorption spectrum of the unmetalated ppy ligand, at 295 nm (1.4 × 10^4 M^{-1} cm^{-1}) and at 240 nm (8 × 10^3 M^{-1} cm^{-1}). The intense ultraviolet absorption bands, observed at 240 and 260 nm in the Rh(III) and Ir(III) dimers, respectively, have extinction coefficients which are about 5 times that of the 295-nm band of ppy, again suggesting rough additivity of four IL transitions in the dimer. In addition to this IL band, both ppy complexes show several transitions between 300 and 500 nm, which are absent in the absorption of the unmetalated ligand. Two shoulders are observed on the 240-nm IL transition of the Rh(III) dimer at 310 and 333 nm. The positions of these bands and their extinction coefficients suggest that they may be MLCT transitions superimposed on the IL band. The well-resolved band at 393 nm, like the 410-nm band of the Rh–bzq complex, red shifts in chloroform, and is assigned as an MLCT transition. A weak but well-resolved band, which is centered at 462 nm, overlaps the emission spectrum and will be considered further in the discussion of emission results below.

Absorption bands at 335 and 355-nm in the Ir(III) dimer are qualitatively similar to the 310- and 333-nm features in the Rh(III) analogue. These bands, as well as additional features at 400 and 434 nm, are assigned to MLCT transitions. A long-wavelength band appearing at 484 nm overlaps the emission spectrum and is considered below.

C. Emission Assignments. The differences in the luminescence lifetimes of the Ir(III) and Rh(III) complexes of each of the two ligands as well as the differences in the energies in their luminescence spectra indicate distinct types of emitting excited states in the complexes of these two metals.

[Rh(bzq)$_2$Cl]$_2$ and [Rh(ppy)$_2$Cl]$_2$. The high-energy features in the phosphorescence of the two unmetalated ligands appear at 480 (bzq) and 440 nm (ppy), as compared to high-energy features at 480 and 460 nm in the emission spectra of their respective Rh(III) complexes. This relatively close correspondence as well as their long emission lifetimes indicate that luminescence originates in triplet intraligand (^{3}IL) states in the Rh(III) dimers. These assignments are further verified by the absence of solvent effects on the emission energies in several low-temperature glasses. The low-energy absorption band at 462 nm in the ppy dimer is interpreted as a direct absorption to the emissive IL triplet. Its extinction coefficient of 48 M^{-1} cm^{-1} is comparable to a similar absorption band recently observed[37] in Rh(bpy)$_3$$^{3+}$; this complex is also known to emit from a ^{3}IL excited state.[38–40] Although no similarly resolved absorption is observed in the bzq dimer, this appears to be due to a relatively intense shoulder at 440 nm which may obscure a low-energy ^{3}IL absorption. This shoulder is thought to arise from an MLCT transition which occurs at lower energy in the bzq complex than in the ppy complex.

[Ir(bzq)$_2$Cl]$_2$ and [Ir(ppy)$_2$Cl]$_2$. In addition to the shorter lifetimes and lower energies of the luminescences of the Ir(III) dimers compared to those of the Rh(III) dimers, the Ir species display relatively intense emissions in ambient fluid solutions as well as solvent-dependent emission energies. These factors indicate MLCT assignments of the luminescent excited states. These assignments also apply to the 480- and 484-nm absorption bands, which, due to their close proximity to the emission bands, appear to represent direct absorptions into the luminescent states. The enhanced extinction coefficients of these bands relative to the 462-nm IL absorption band of [Rh(ppy)$_2$Cl]$_2$ are consistent with

larger spin–orbit coupling terms anticipated for the MLCT states than for the IL excited state. The 440-nm absorption feature of [Rh(bzq)$_2$Cl]$_2$, assigned as a MLCT band, has an extinction coefficient comparable to the long-wavelength absorption bands of the two Ir(III) dimers, consistent with these interpretations.

V. Summary and Conclusions

It is informative to compare the present results with results from previous studies of bpy and phen complexes of Rh(III) and Ir(III) in order to gain some insights into the effects of M–C bonds in comparison to M–N bonds in otherwise similar complexes. The basic thermal chemistry of the ppy and bzq ligands with these metals is distinct from that of bpy and phen. The former ligands have a strong tendency to form dichloro-bridged species in reactions with metal chlorides, whereas the latter are known to form mononuclear species under similar reaction conditions. Although a dichloro-bridged complex of Ru(II) has been prepared,[18] it is formed under carefully controlled conditions where the amount of available chloride is limited to 1 mol per mol of Ru(II) and only weakly ligating solvent molecules are available for potential cleavage of the dichloro bridge. Reactions of bpy or phen with chlorides of Ru(II) more generally yield mononuclear products analogous to those formed in reactions of Rh(III) and Ir(III). The tendency of ppy and bzq to form bridged species may be viewed as a result of the enhanced electron density at the metal center imposed by larger σ donation through the M–C bond than would be the case in M–N bonded complexes of bpy and phen. Consideration of the bridged dimers as M(III) bonded to anionic ppy$^-$ or bzq$^-$ ligands leads to a formal count of 16 electrons on each of the M(III) centers as compared to an 18-electron count in mononuclear species of the type ML$_2$Cl$_2$$^+$ [M = Rh(III), Ir(III); L = bpy, phen] and a 16-electron count in mononuclear complexes of Rh(I) or Ir(I) such as Rh(bpy)$_2$$^+$. This point of view suggests that the bridged dimers contain metal centers with an electron density intermediate between M(I) and M(III) in mononuclear bpy and phen complexes, consistent with the reactivity intermediate between the strong tendency of Rh(bpy)$_2$$^+$ to undergo oxidative addition reactions and the relatively inert character of Rh(bpy)$_3$$^{3+}$ toward thermal reduction. The participation of the dimers in bridge cleavage reactions, particularly with good π-acceptor ligands, to yield mononuclear species with a formal 18-electron count, reflects this intermediacy in their reactivities.

In addition to affecting ground-state reactivities, enhanced metal electron density due to σ donation through the M–C bonds should have significant effects on MLCT and LF excited states in the dimers relative to the M–N bonded mononuclear bpy and phen complexes. Several of our observations illustrate that these effects do indeed occur and that they are quite significant. Perhaps the most striking of these effects is illustrated by comparison of the emission spectra of [Rh(ppy)$_2$Cl]$_2$ and [Rh(bzq)$_2$Cl]$_2$ with those of Rh(bpy)$_2$Cl$_2$$^+$ and Rh(phen)$_2$Cl$_2$$^+$. Both the bpy and phen complexes show[38–40] a characteristic broad LF emission in the red region, in contrast to the structured blue IL emissions of the ppy and bzq dimers. This suggests a downward movement of the IL triplets in the ppy and bzq complexes and/or an increase in the energies of the LF states relative to the bpy and phen complexes. Comparison of the triplet IL-state energies in the Rh–N,N and Rh–N,C bonded complexes can be accomplished by reference to the emission energies of Rh(bpy)$_3$$^{3+}$ and Rh(phen)$_3$$^{3+}$, which both display ^{3}IL emissions originating at 450 nm.[38–40] The ^{3}IL emissions of the two dimers (460 nm, ppy; 480 nm, bzq) are slightly lower in energy but well above the estimated ^{3}LF-state energies (1.68 μm^{-1}, 595 nm) taken from emission maxima and Stokes shift data for Rh(bpy)$_2$Cl$_2$$^+$ and Rh(phen)$_2$Cl$_2$$^+$.[38] The occurrence of ^{3}IL emissions in the ppy and bzq dimers must arise, therefore, primarily from large increases in the ligand field splitting parameter which shifts the ^{3}LF states above the ^{3}IL states. Use of the ^{3}IL emission energies of the dimers with a correction to account for the absence of any apparent thermal population of ^{3}LF states suggests a minimum 0–0 energy for the lowest ^{3}LF excited states in the dimers of about 2.2 μm^{-1}. Application of the method of Carstens and Crosby[38] for determination of the average crystal

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field splitting parameter Δ_{av} yields a value of 3.41 μm^{-1}. Using a value for the Jørgenson metal g value for Rh(III) of 2.7 μm^{-1} yields a minimum ligand f value of 1.5 for the ppy and bzq ligands. Due to the use of a minimum ^{3}LF energy and a probable overestimate of the contributions of bridging chlorides[41] to the average crystal field splitting parameter, this ligand f value represents a lower limit. However, it is clear from this estimate that ppy and bzq lie well above bpy and phen ($f = 1.33$) in the spectrochemical series.

This position indicates that the low-energy LF states which contribute to dual LF/MLCT emissions[42-45] of $IrCl_2(bpy)_2^+$ and $IrCl_2(phen)_2^+$ should make no contributions to the emissions of the Ir(III) dimers of the former ligands. Indeed, no evidence for LF emissions is found in these complexes. The observed MLCT emissions of the ppy and bzq dimers (490 and 510 nm, respectively) lie well below the MLCT components of the $IrCl_2(bpy)_2^+$ and $IrCl_2(phen)_2^+$ emissions (475 nm, both), as expected. This enhancement in the MLCT character of the lowest excited states of the dimers should decrease deactivation through LF excited states, which often takes the form of ligand labilization,[46-49] and

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improve the efficiency with which they participate in photoredox processes. A study of their electrochemical and photoredox properties is presently in progress.

The overall view of the spectroscopic effects of ppy and bzq as bidentate ligands with Rh(III) and Ir(III) which derives from the above considerations is a remarkable one. The relatively low energy MLCT emissions observed for their Ir(III) complexes indicate that they are good π-accepting ligands with sufficiently delocalized π^* orbitals to accomodate electron transfer from the Ir(III) metal center in the excited state. They are further sufficiently strong σ donors, largely through their Ir–C bonding, to enrich the electron density of Ir(III) sufficiently to render the metal somewhat more oxidizable than it is in comparable bpy and phen complexes. This synergistic combination of bonding effects is not sufficient to induce an MLCT emission in the Rh(III) dimers, but relatively intense absorption bands in these species in the region around 400 nm are assigned as MLCT transitions. Comparable bands are not seen in the absorption spectra of similar bpy and phen complexes of Rh(III), where they are probably buried at higher energies under the intense $\pi-\pi^*$ ligand-centered absorptions. These spectroscopic results suggest that enhancement of the electron density at metal centers via metal–carbon σ bonding to π-conjugated ligands such as ppy and bzq may add new dimensions to the electrochemical and photochemical properties of the resultant complexes relative to those of fully N-coordinated bpy and phen complexes.

Picosecond Photolysis of Axial Ligands on Cobalt(II) and Cobalt(III) Porphyrins

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Abstract: Excited-state photoprocesses of cobalt(II) octaethylporphyrin (OEP), cobalt(II) tetraphenylporphyrin (TPP), Co^{III}(OEP)(CN), and Co^{II}(OEP)(CN)(γ-picoline) in noncomplexing solvents and in the presence of coordinating species Me$_2$SO and piperidine have been studied. The transient absorption spectra suggest that the excited-state relaxation of cobalt(II) porphyrins proceeds via the tripdoublet, $^2T(\pi, \pi^*)$, and the $^2(\pi, d_{z^2})$ charge-transfer (CT) states and that rapid deactivation of the latter state competes favorably with axial ligand release, accounting for the low yield for photodissociation. When five-coordinate Co^{III}(OEP)(CN) is excited, the transient spectra suggest that the initial (π, π^*) and (π, d) CT excited states decay to $^3(d_\pi, d_{z^2})$, followed by ligand loss to produce four-coordinate [Co^{III}(OEP)]$^+$. However, when six-coordinate [Co^{III}(OEP)L$_2$]$^+$ systems are excited, the transient spectra suggest that both five-coordinate [Co^{III}(OEP)L]$^+$ and four-coordinate [Co^{III}(OEP)]$^+$ are produced, both presumably from $^3(d_\pi, d_{z^2})$, which is not observed. In 1–4 M ligating solvents [Co^{III}(OEP)L]$^+$ rebinds a ligand in 250 ps to 1.4 ns, whereas [Co^{III}(OEP)]$^+$ is stable for ≥ 1 ns. This difference in stability is attributed to the five-coordinate species having a singlet ground state, while the four-coordinate species is a triplet ligand-field (d, d) state.

Binding and release of ligands from the iron porphyrin active site of hemoglobin and myoglobin are of considerable biological significance. While iron porphyrins are frequently used as synthetic model systems, cobalt(II) porphyrins are also known to bind O$_2$ and CO.[1-3] Cobalt(III) porphyrins exhibit catalase-like activity in the disproportionation of H$_2$O$_2$.[4]

A study of the photorelease of basic axial ligands from five-coordinate cobalt(II) deuteroporphyrin IX dimethyl ester

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