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Excited-State Properties of Binuclear Group 6B Metal Carbonyl Complexes. Emission and Photochemistry in Fluid Solution[1]

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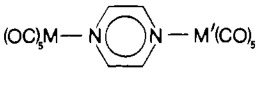
Synthetic routes to homonuclear and heteronuclear dimer metal carbonyl complexes, $(OC)_5M(pyz)M'(CO)_5$, where M, M' = Cr, Mo, W and pyz = pyrazine, are described. Each complex exhibits low-lying ligand field (LF) and metal to ligand charge-transfer (MLCT) absorptions that are well separated in energy. The energy of the MLCT transition is shown to be extremely solvent sensitive. The emission and photochemical properties of the LF and MLCT states have been independently characterized. Each complex is observed to emit in solution at 283–298 K in the 550–850-nm region; the low-energy metal $\rightarrow \pi^*$(pyz) excited state is inferred to be the emitting state. Direct irradiation (λ = 395 nm) into the LF absorption band of $(OC)_5W(pyz)W(CO)_5$ results in W–N bond cleavage to form mononuclear products with a photochemical quantum efficiency of 0.042 at 293 K. In contrast direct irradiation into the W $\rightarrow \pi^*$(pyz) absorption of $(OC)_5W(pyz)W(CO)_5$ results in W–N bond cleavage of much reduced quantum efficiency, 0.0013. An excited-state scheme for $(OC)_5M(pyz)M'(CO)_5$ is presented.

Introduction

The photochemical properties of transition-metal complexes that possess low-energy metal to ligand charge-transfer (MLCT) excited states have been extensively investigated.[2,3] In a series of recent papers we have reported on the emission and photochemical behavior of several classes of mononuclear group 6B metal carbonyl complexes in room-temperature solution.[4] For each complex the room-temperature emission has been associated with the presence of a low-lying MLCT state. It has also been noted that the complexes that undergo emission under normally photochemical conditions exhibit much reduced photoreactivities. In contrast closely related complexes in which a ligand field (LF) state is the lowest energy electronically excited state do not give rise to observable emission in room-temperature solution and on excitation proceed with substantially greater photoreactivities. Binuclear complexes of the formula $(OC)_5M(pyz)M(CO)_5$ where M = Cr, Mo, W and pyz = pyrazine, are of particular interest in this respect as their lowest energy excited states are clearly MLCT, due to the low-lying π^*-acceptor orbitals of the pyrazine ligand.[5-7] The MLCT states of these binuclear complexes are so well separated from the higher energy LF states that their photochemical properties can be studied exclusively. In contrast to the excited-state properties of mononuclear metal carbonyl complexes, those of binuclear metal carbonyls remain relatively unexplored.[8] It is also of considerable interest that these binuclear metal carbonyl complexes are isoelectronic with the well-known $[(H_3N)_5Ru(pyz)Ru(NH_3)_5]^{4+}$ complexes investigated by Creutz and Taube.[9] This paper reports the results of our study of the excited state properties of $(OC)_5M(pyz)M'(CO)_5$ complexes and includes the novel heteronuclear (M ≠ M') dimer compounds.



M,M' = Cr, Mo, W

Experimental Section

Materials. The metal hexacarbonyls (Strem Chemicals) and pyrazine (Aldrich Chemical Co.) were used without further purification. Benzene, isooctane, and hexane were spectroscopic grade (MCB Manufacturing Chemists); the other solvents used were reagent grade. The solvents used in emission experiments were distilled several times to ensure removal of impurities. All tetrahydrofuran (THF) used was distilled from $LiAlH_4$ and stored under argon. Alumina (80–200 mesh, Fisher Scientific Co.) was used for column chromatography.

Synthesis. The $M(CO)_5pyz$ complexes were isolated by reacting ~2 mmol of photoproduced $M(CO)_5THF$ with 3 mmol of pyrazine under an argon atmosphere. The solvent adduct $M(CO)_5THF$ was obtained by photolysis of 3 mmol of $M(CO)_6$ in argon-purged THF and was not isolated. The THF was removed by rotary evaporation, and the solid product was redissolved in hexane and purified by column chromatography on alumina. The main impurities were found to be $M(CO)_6$ and L. Elution was first with hexane until the UV absorption features of $M(CO)_6$ could no longer be detected in the eluate, followed by elution of $M(CO)_5pyz$ with benzene. The product was recovered by rotary evaporation and further purified by recrystallization if necessary. Infrared and UV–vis absorption spectra of $M(CO)_5pyz$ agreed well with those previously reported.[10]

The $(OC)_5M(pyz)M'(CO)_5$ complexes were obtained by thermally reacting approximately equimolar amounts of $M(CO)_5pyz$ with prior photogenerated $M'(CO)_5THF$ in argon-purged hexane containing 0.1 M THF. The products were collected by suction filtration and washed repeatedly with hexane under an atmosphere of argon. The binuclear complexes, where M = M', were also synthesized by direct 313-nm photolysis of 4 mmol of $M(CO)_6$ in argon-purged hexane containing 2 mmol of pyrazine. The products were purified by repeated washings

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Table I. Carbonyl Infrared Stretching Frequencies and Assignments for the $(OC)_5M(pyz)M'(CO)_5$ Complexes[a]

complex M, M'	bands, cm^{-1} $A_1{}^2$	B_2	E	$A_1{}^1$
Cr, Cr	2070	1965	1942, 1920	1895
Cr, Mo	2070	1965	1945, 1920	1895
Mo, Mo	2075	1965	1950, 1922	1895
Mo, W	2075	1965	1945, 1920	1892
W, W	2075	1960	1940, 1915	1892
W, Cr	2070	1963	1940, 1917	1895

[a] In Nujol mulls at 298 K.

with hexane followed by column chromatography on alumina under an argon atmosphere.

The $(OC)_5M(pyz)M'(CO)_5$ complexes were moderately stable in the solid from and were kept in the dark at 273 K; storing under argon greatly increased their long-term stability. The chromium complexes were particularly susceptible to oxidation on exposure to air and were handled under an argon environment. In solution at 298 K the complexes exhibited varying degrees of stability, with the chromium and molybdenum complexes exhibiting the fastest decomposition.

Elemental analyses are as follows. Anal. Calcd for $(OC)_5Cr(pyz)Cr(CO)_5$: C, 36.23; H, 0.87; N, 6.03. Found: C, 36.02; H, 0.94; N, 6.14. Calcd for $(OC)_5Cr(pyz)Mo(CO)_5$: C, 33.09, H, 0.79; N, 5.51. Found: C, 33.23; H, 0.88; N, 5.43. Calcd for $(OC)_5Mo(pyz)Mo(CO)_5$: C, 30.46; H, 0.73; N, 5.07. Found: C, 30.65; H, 0.63; N, 5.40. Calcd for $(OC)_5Mo(pyz)W(CO)_5$: C, 26.27; H, 0.63; N, 4.38. Found: C, 26.49; H, 0.65; N, 4.02. Calcd for $(OC)_5W(pyz)W(CO)_5$: C, 23.10; H, 0.55; N, 3.85. Found: C, 22.83; H, 0.51; N, 3.62. Calcd for $(CO)_5W(pyz)Cr(CO)_5$: C, 28.21; H, 0.68; N, 4.70. Found: C, 28.54; H, 0.84; N, 4.53. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA.

Spectra. Infrared spectra were recorded from the complexes as Nujol mulls between NaCl plates on a Perkin-Elmer Model 283B spectrometer. Electronic absorption spectra were obtained on a Hewlett-Packard 8450A spectrophotometer, which incorporates a microprocessor-controlled diode-array detector. This permitted absorption spectral data to be obtained from the thermally sensitive complexes within 5 s of dissolution. Emission spectra were recorded from filtered argon-purged solutions of $(OC)_5M(pyz)M'(CO)_5$ with a Perkin-Elmer MPF-44B spectrofluorometer and were corrected for variation in instrumental response as a function of wavelength. Emission band maxima are considered to be accurate to ±10 nm. Emission quantum yields were determined with the use of a known emitter, $Ru(bpy)_3{}^{2+}$,[11] and are considered accurate to ±15%.

Photolyses. All photolysis experiments were carried out with an Ealing Corporation 200-W mercury-xenon arc lamp with Baird-Atomic and Rolyn Optics Corp. interference filters (10 nm band-pass) to isolate the irradiation wavelengths at 395, 430, and 465 nm. Typical light intensities were 10^{-9}–10^{-8} einstein s^{-1} determined by ferrioxalate[12] (395 and 430 nm) or Reineckate[13] (465 nm) actinometry. A Lexel Corp. Model 95-4 argon ion laser was used to perform the 514-nm photolyses. The typical laser power for the 514-nm excitation was 200 mW. The photon flux was calculated from the laser power, measured by means of an external Lexel Corp. Model 504 power meter. The incident light intensities were further measured by Reineckate actinometry. Sample solutions ($\sim 10^{-4}$ M) were filtered through a 0.22-μm Millipore filter immediately before use and transferred to a 1 × 1 cm four-clear-sided quartz cell. The solutions were deaerated by argon purging for 20 min. The solution temperature was controlled to ±0.1 K by circulating thermostated water. In all photolysis experiments the concentrations of reactants and products were followed by UV-vis spectroscopy. Quantum yield measurements were made for disappearance of starting material in the 500–600-nm region. They were corrected for the small inner filter effects due to product formation and changing degree of light absorption when necessary. For 395- and 430-nm photolyses the measurements were made over relatively small conversions. Reproducibility of quantum yields was within ±10%.

Table II. Electronic Absorption Spectra of $(OC)_5M(pyz)M'(CO)_5$ Complexes in Benzene (Isooctane) at 298 K[a]

complex M, M'	band maxima λ, nm LF	MLCT
Cr, Cr	408 (408)	516 (572)
Cr, Mo	395 (400)	504 (562)
Mo, Mo	388 (388)	484 (536)
Mo, W	392 (392)	498 (544, 573)
W, W	397 (397)	510 (552, 595)
W, Cr	399 (399)	514 (548,[b] 586)

[a] Spectral data recorded within 5 s of dissolution. [b] Observed as a shoulder.

Results and Discussion

Synthesis of $(OC)_5M(pyz)M'(CO)_5$. The binuclear complexes were prepared according to the following procedure. First, $M(CO)_5pyz$, M = Cr, Mo, W, complexes were synthesized via the corresponding tetrahydrofuran complex, $M(CO)_5THF$ (reactions 1 and 2), according to an established literature method.[6] The $M(CO)_5pyz$ complexes were subsequently thermally reacted with photochemically generated $M'(CO)_5THF$[14] (reactions 3 and 4). This reaction was carried

$$M(CO)_6 \xrightarrow[\text{Ar-purged THF}]{h\nu,\ \lambda = 313\ \text{nm}} M(CO)_5THF + CO \qquad (1)$$

$$M(CO)_5THF \xrightarrow[\text{pyz}]{\Delta} M(CO)_5pyz + THF \qquad (2)$$

$$M'(CO)_6 \xrightarrow[\text{Ar-purged hexane + 0.1 M THF}]{h\nu,\ \lambda = 313\ \text{nm}} M'(CO)_5THF + CO \qquad (3)$$

$$M'(CO)_5THF \xrightarrow[M(CO)_5pyz]{\Delta} (OC)_5M(pyz)M'(CO)_5 + THF \qquad (4)$$

out in hexane containing 0.1 M THF, rather than THF, to avoid thermal decomposition of $(OC)_5M(pyz)M'(CO)_5$, which occurs in polar solutions. In hexane the binuclear products are virtually insoluble and precipitate out of solution.

An alternative route was found to yield the $(OC)_5M(pyz)M'(CO)_5$ complexes, where M = M' (reaction 5). The

$$2M(CO)_6 \xrightarrow[\text{pyz + Ar-purged hexane}]{h\nu,\ \lambda = 313\ \text{nm}} M(CO)_5pyz + M(CO)_5 + 2CO \xrightarrow{\Delta} (OC)_5M(pyz)M(CO)_5 \qquad (5)$$

initial photoproducts, $M(CO)_5pyz$ and $M(CO)_5$, immediately combine to form $(OC)_5M(pyz)M(CO)_5$, which precipitates out of solution. The formation of $M(CO)_5pyz$ during this reaction was confirmed by UV-visible spectroscopy. The other primary photoproduct is presumably an unsaturated $M(CO)_5$ species (recent literature reports indicate that this would probably exist as $M(CO)_5C_6H_{14}$[15]) which reacts rapidly with $M(CO)_5pyz$ to form the binuclear product.

Infrared Spectra. The infrared carbonyl stretching frequencies obtained from the series of $(OC)_5M(pyz)M'(CO)_5$ complexes as Nujol mulls are listed in Table I. The carbonyl stretching frequencies are close to those previously reported for $M(CO)_5pyz$ complexes,[10] indicating that the local C_{4v} symmetry of the $M(CO)_5$ groups in $(OC)_5M(pyz)M'(CO)_5$ is preserved.

Electronic Absorption Spectra. The $(OC)_5M(pyz)M'(CO)_5$ complexes were observed to exhibit varying degrees of stability in solution. The mechanism of this thermal reaction has been

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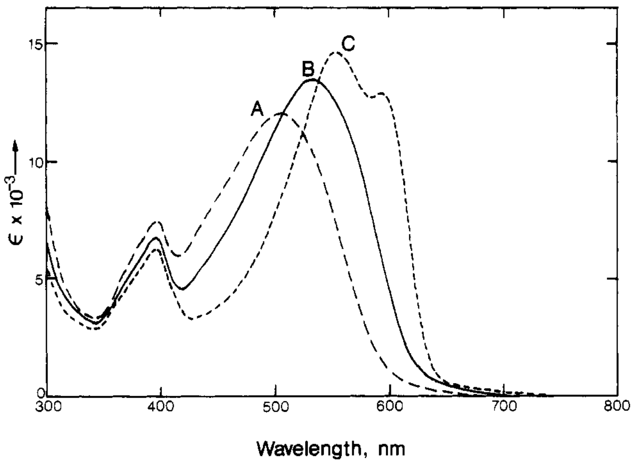

Figure 1. Electronic absorption spectra at 298 K of $(OC)_5W(pyz)W(CO)_5$ in (A) benzene, (B) benzene–isooctane (1:10 v/v), and (C) isooctane.

reported in the literature.[5] Accurate absorption data was obtained by recording spectra within 5 s of dissolution of the complex with a microprocessor-controlled diode-array spectrophotometer.

The electronic absorption spectra of $(OC)_5W(pyz)W(CO)_5$ in benzene, benzene–isooctane (1:10 v/v), and isooctane are shown in Figure 1. Absorption data obtained from all the binuclear complexes studied are summarized in Table II. An assignment of the electronic spectra of these $(OC)_5M(pyz)M'(CO)_5$ complexes is made relatively simple due to the well-characterized spectra of the pyridine derivatives of mononuclear group 6B metal carbonyl complexes.[3f,16] Each complex exhibits a characteristic absorption maximum in the 385–410-nm region that is assigned to a ligand field (LF) ${}^1A_1(e^4b_2{}^2) \rightarrow {}^1E(e^3b_2{}^2a_1{}^1)$ transition. This transition is at approximately the same energy in the absorption spectra of the corresponding $M(CO)_5pyz$ complexes,[9,16c] further indicating that the local C_{4v} symmetry of the $M(CO)_5$ groups in $(OC)_5M(pyz)M'(CO)_5$ is retained. The LF transition is characteristically not solvent dependent[17] (see Figure 1 and Table II). In contrast the low-energy absorption maximum for each complex in the 480–520-nm region is extremely solvent sensitive and is assigned to a M → π^*(pyz) charge-transfer transition. This transition is at considerably lower energy than that for the corresponding $M(CO)_5pyz$ complexes;[9,16c] the energies of the π^*-acceptor orbitals on pyrazine are therefore effectively lowered as this ligand binucleates (see Figure 2). Apparently this is a substantial effect; the MLCT energies for $(CO)_5M(pyz)M'(CO)_5$ are comparable to those for mononuclear complexes in which two CO ligands have been replaced, e.g., $M(CO)_4L$, where L is 2,2′-bipyridine, 1,10-phenanthroline, diazabutadiene, or derivatives,[17,18] and *cis*-$M(CO)_4L_2$, where L is a pyridine ligand with a strongly electron-withdrawing substituent.[19] Furthermore the MLCT states of the complexes reported here are of considerably lower energy than those observed from closely related $[W(CO)_5]_2L$ complexes, where L is 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene.[20]

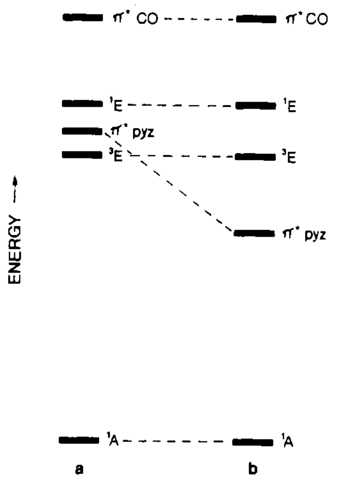

Figure 2. Relative energies of the excited states observed in the absorption spectra of (a) $M(CO)_5pyz$[10] and (b) $(OC)_5M(pyz)M'(CO)_5$. The ${}^1A \rightarrow {}^3E$ transition is not observed in the spectra of $(OC)_5M(pyz)M'(CO)_5$, but its energy is assumed to be unshifted from that of $M(CO)_5pyz$.

Table III. Solvent Effects on Absorption Band Maxima of $(OC)_5W(pyz)W(CO)_5$ at 298 K[a]

solvent	band maxima λ, nm LF	MLCT
dimethyl sulfoxide	395	442
dimethylformamide	395	446
acetone	395	460
cyclohexanone	395	468
methanol	395	476
tetrahydrofuran	395	480
cyclohexanol	395	492
piperidine	395	500
benzene	397	510
methylene chloride	395	521
triethylamine	395	523
mesitylene	395	529
carbon tetrachloride	396	548, 590[b]
tetrachloroethylene	397	550, 590[b]
isooctane	396	552, 595

[a] Spectra were recorded within 5 s of dissolution to minimize thermal decomposition effects. [b] Observed as a shoulder.

The $(OC)_5W(pyz)W(CO)_5$ complex is considerably more stable in solution than the others of this series, and absorption data have been obtained in a wide variety of solvents. Table III illustrates the solvent sensitivities of the LF and MLCT transitions; the former absorption is relatively unaffected by the nature of solvent medium, whereas the latter substantially red shifts as the solvent becomes less polar.

We wish to draw attention to the band structure of the low-energy MLCT absorption. For $(OC)_5W(pyz)W(CO)_5$ in benzene this absorption is noticeably asymmetrical (Figure 1). In isooctane, however, the MLCT absorption red shifts considerably and clearly shows the presence of two M → π^*(pyz) components. Similarly resolved features have been observed for $(OC)_5W(pyz)W(CO)_5$ in carbon tetrachloride and tetrachloroethylene (Table III) and for other complexes of this series in isooctane (Table II). Recent resonance Raman measurements have indicated that the low-energy absorption envelope of $(OC)_5W(pyz)W(CO)_5$ comprises several MLCT transitions, of which two have been assigned to be symmetry-allowed *y*- and *z*-polarized transitions.[7]

Emission Spectra. Each complex was observed to exhibit broad, unstructured emission in the 550–800-nm region; rep-

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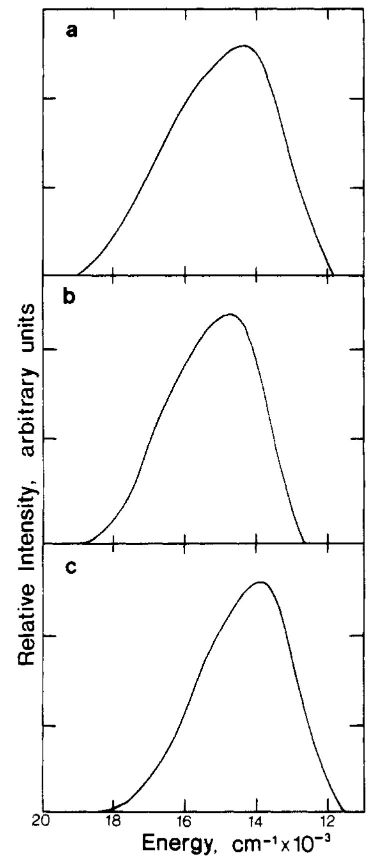

Figure 3. Corrected emission spectra of (a) $(OC)_5Cr(pyz)Cr(CO)_5$, (b) $(OC)_5Mo(pyz)Mo(CO)_5$, and (c) $(OC)_5W(pyz)W(CO)_5$ in benzene at 283 K. Intensities are scaled to make maxima equal. Excitation wavelength is 400 nm.

Table IV. Emission Spectral Data of $(OC)_5M(pyz)M'(CO)_5$ in Benzene at 283 K[a,b]

complex M, M'	emission[c] maxima, nm	half-width,[d] $cm^{-1} \times 10^3$	$10^4 \times$ quantum yield[e]
Cr, Cr	702	3.7	0.6 (0.7)
Cr, Mo	687	3.9	1.4 (1.7)
Mo, Mo	675	3.8	3.9 (4.6)
Mo, W	712	2.9	4.6 (5.5)
W, W	722	3.5	5.0 (6.2)
W, Cr	707	3.5	1.5 (2.0)

[a] Recorded at 298 K for $(OC)_5W(pyz)W(CO)_5$. [b] 8×10^{-5}–2×10^{-4} M deaerated solutions. [c] Spectra were corrected for variation in instrumental response as a function of wavelength. The excitation wavelength is 400 nm. [d] Width of emission band at half-height. [e] Measured relative to the emission of $Ru(bpy)_3^{2+}$; accurate to within ±15%. Data in parentheses are yields determined following MLCT excitation (λ = 500 nm).

resentative spectra are shown in Figure 3. The data from all the binuclear complexes are summarized in Table IV. Emission spectra were recorded at 283 K to minimize thermal reaction. The spectral distribution of the emission from each complex was observed to be independent of excitation wavelengths longer than 300 nm, which is consistent with emission from a single low-lying excited state. The onset of emission in the 550–600-nm region leads us to assign the emission of each complex to the lowest energy M → π*(pyz) excited state. This is analogous to the MLCT emission that has previously been observed from $M(CO)_5L$ and *cis*-$M(CO)_4L_2$ complexes, where M = Cr, Mo, W and L = a pyridine derivative.[4] However, the $(OC)_5M(pyz)M'(CO)_5$ complexes represent the first binuclear group 6B metal carbonyl complexes known to emit in fluid solution. Emission quantum yields for the binuclear complexes are reported in Table IV. The emission quantum efficiency for $(OC)_5W(pyz)W(CO)_5$ was observed to be independent of temperature throughout the 283–303 K range, indicating that the emission process is not a thermally activated one.

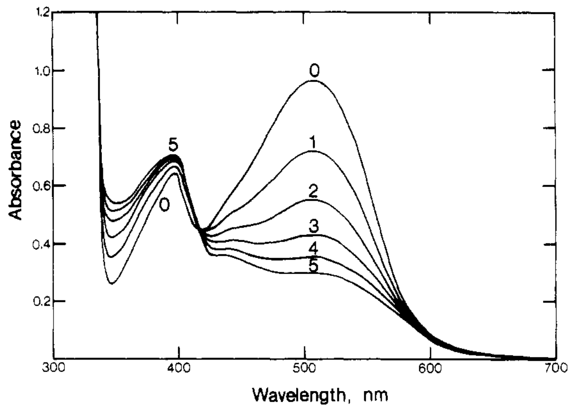

Figure 4. Electronic absorption spectral changes accompanying the 514-nm photolysis (equal time intervals) of 7.8×10^{-5} M $(OC)_5W(pyz)W(CO)_5$ in benzene containing 0.1 M pyrazine at 293 K.

The corresponding $M(CO)_5pyz$ complexes (M = Cr, Mo, W) were not observed to emit under identical conditions. This result is consistent with those previously obtained from other classes of substituted metal carbonyl complexes where a ligand field transition is the lowest-lying one.[4]

Photochemistry. Only the $(OC)_5W(pyz)W(CO)_5$ complex was sufficiently stable thermally to obtain accurate photochemical data. Photolysis into the low-lying W → π*(pyz) absorption of $(OC)_5W(pyz)W(CO)_5$ breaks the W–pyz bond. In the presence of excess pyrazine as scavenging ligand the reaction proceeds to form mononuclear $W(CO)_5pyz$ products (reaction 6). Figure 4 illustrates the typical spectral sequence

$$(OC)_5W(pyz)W(CO)_5 \xrightarrow[0.1\ M\ pyz,\ C_6H_6]{h\nu,\ \lambda} 2W(CO)_5pyz \qquad (6)$$

$$\lambda = 395,\ 430,\ 465,\ 514\ nm$$

observed during the 514-nm photolysis of $(OC)_5W(pyz)W(CO)_5$ in benzene showing the progression to the spectrum of $W(CO)_5pyz$. An isosbestic point at 418 nm was retained during long-wavelength photolyses throughout >70% conversions, indicating that over this period the reaction appears to be uncomplicated by side or subsequent reactions. This was the only reaction that we observed at all of the excitation wavelengths, and no evidence was found for photodissociation of CO. We infer that the primary photoreaction of $(OC)_5W(pyz)W(CO)_5$ is cleavage of the W–N bond to form $W(CO)_5pyz$ and $W(CO)_5$, the latter species being rapidly scavenged in the presence of excess pyrazine to form a second molecule of $W(CO)_5pyz$. The thermal decomposition of $(OC)_5Mo(pyz)Mo(CO)_5$ in the presence of pyrazine has also been reported to proceed by this route, and the kinetic events have been described in detail.[5] In the absence of pyrazine the photochemistry is complicated, and an early loss of isosbestic point was observed on photolysis. Although $W(CO)_5pyz$ is presumably still produced, further conjugated species such as $[W(CO)_5]_n$ may also be formed. Similar observations have been made in the thermal study of $(OC)_5Mo(pyz)Mo(CO)_5$.[5]

As previously noted, the LF and M → π*(pyz) absorptions of these binuclear complexes are unusually well separated in energy. The relative photoefficiencies of these states have been measured through a wavelength-dependence study; these results are reported in Table V. Excitation at 514 nm can be assumed to exclusively populate the W → π*(pyz) state of $(OC)_5W(pyz)W(CO)_5$. This state can be concluded to be virtually unreactive. In contrast, excitation at 395 nm popu-

Table V. Wavelength Dependence of Photodissociation Quantum Yields for $(OC)_5W(pyz)W(CO)_5$ in Benzene Containing 0.1 M Pyrazine

irradiation wavelength, nm	quantum yield[a]	irradiation wavelength, nm	quantum yield[a]
395	0.042	465	0.007
430	0.030	514	0.001

[a] Recorded at 293 K.

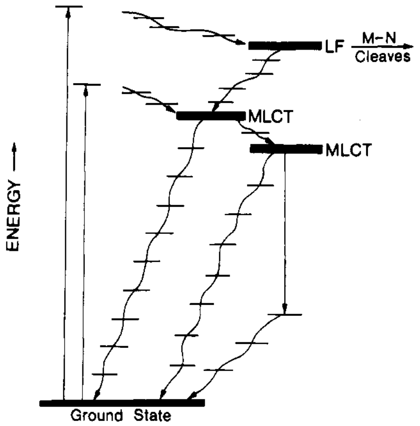

Figure 5. Excited-state scheme for $(OC)_5M(pyz)M'(CO)_5$ complexes, M, M′ = Cr, Mo, W. Vertical and wavy lines represent radiative and nonradiative processes, respectively. Heavy horizontal lines depict thermally equilibrated excited states. Light horizontal lines represent successive complex–solvent cage energies as vibrationally excited states relax (only a few of these lines are shown).

lates the LF state, from which photoreaction proceeds with significantly higher quantum efficiency. The relative reaction efficiencies of the LF and W → π^*(pyz) excited states of $(OC)_5W(pyz)W(CO)_5$ are characteristic of those obtained from closely related mononuclear metal carbonyl complexes in which the MLCT state lies below the LF state.[4a]

The temperature dependency of the photoreaction efficiency of $(OC)_5W(pyz)W(CO)_5$ was investigated for LF (395 nm) and W → π^*(pyz) (514 nm) excitations. For LF excitation photodissociation quantum yields determined at 283, 288, 293, 298, and 303 K are 0.039, 0.043, 0.042, 0.046, and 0.049, respectively. The least-squares line of an Arrhenius type plot (ln ϕ vs. $1/T$) of these data corresponds to an apparent activation energy of 1.9 (±1) kcal mol^{-1}. This low value indicates that the photoreaction of $(OC)_5W(pyz)W(CO)_5$ is not thermally activated to higher energy states and proceeds directly from the LF state. For W → π^*(pyz) excitation the quantum yields at the above temperatures are 0.0011, 0.0012, 0.0013, 0.0013, and 0.0014, respectively. Here the least-squares line of an Arrhenius type plot corresponds to an apparent activation energy of 1.9 (±1) kcal mol^{-1}. This result implies that the MLCT state does not significantly thermally populate the LF state and importantly that the MLCT state is intrinsically photoreactive, albeit very inefficiently.

Summary

The experimental observations are summarized in an excited-state scheme for $(OC)_5M(pyz)M'(CO)_5$ (Figure 5). The relative positions of the LF and M → π^*(pyz) states identified in the electronic absorption spectra are depicted in the scheme. A $^1A \rightarrow {}^3E$ state is not included in this excited-state scheme; this transition is predicted to be very weak ($\epsilon \approx 500$)[10] and is obscured by the more intense $^1A \rightarrow {}^1E$ and M → π^*(pyz) transitions. As a consequence we were unable to populate this excited state to an appreciable extent to characterize its emission and photochemical properties.

Direct excitation into the LF state of each complex yields emission in the 550–850-nm region. For each complex the emission was assigned to the M → π^*(pyz) excited state; the vertical line from this state denotes this process. The LF state of $(OC)_5M(pyz)M'(CO)_5$ thus populates the emitting state by nonradiative processes; the wavy line between these states denotes this process. Each complex exhibited a single unstructured emission band; the clear inference is that the low-lying M → π^*(pyz) states are in thermal equilibrium with each other. The emission is assigned to the lower energy MLCT component.

The photochemical findings are expressed in the excited-state scheme. Chemical reaction (M–N dissociation) was observed to occur relatively efficiently from the higher energy LF state, whereas the low-energy M → π^*(pyz) excited states are, in contrast, virtually unreactive.

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Characterization of a Stable Chromium(III)–Nicotinic Acid Complex by Deuteron NMR

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The first carboxyl-bound nicotinic acid complex of chromium(III), *trans*-$[Cr(1,3\text{-pn})_2(\text{nic-O})_2]Cl$, which is stable in aqueous solution at physiological pH has been synthesized. The stability and the identity of the complex have been established by deuteron NMR obtained for this complex with deuterium-labeled nicotinic acid. The deuteron NMR spectral data are also provided for previously reported chromium(III) nicotinate complexes having both carboxyl and pyridyl nitrogen coordination to chromium(III). The variation in chemical shifts with these different modes of coordination provides a direct method for determining coordination to chromium(III) in solution.

Nicotinic acid (niacin) complexes of chromium(III) are of current interest since chromium has been shown to be an essential trace element associated with glucose metabolism.[1] Nicotinic acid has been found with chromium in natural

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