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Multiple-State Emission from Ligand-Bridged $(OC)_5W-L-W(CO)_5$ Complexes

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Electronic absorption and photophysical properties are reported for a series of ligand-bridged $(OC)_5W-L-W(CO)_5$ complexes and their corresponding mononuclear derivatives in fluid hydrocarbon solutions and 2-methyltetrahydrofuran (2-MeTHF) glasses at 80 K. The bridging ligands are pyrazine (pyz), 4,4′-bipyridine (bpy), *trans*-1,2-bis(4-pyridyl)ethylene (bpe), and 1,2-bis(4-pyridyl)ethane (bpa). Emission spectra, quantum yields, and lifetimes of the binuclear $(OC)_5W-L-W(CO)_5$ (L = pyz, bpy, bpe) complexes in room-temperature solution indicate two distinct emitting levels that are assigned to triplet-centered *y*- and *z*-polarized metal to ligand charge-transfer (^{3}MLCT) excited states. Temperature and excitation wavelength effects on the emission spectra and lifetimes illustrate that these two ^{3}MLCT excited states are thermally equilibrated in fluid solution; the emission data are fitted to a Boltzmann model placing the energy gap between the ^{3}MLCT levels at 370 (±85) cm^{-1}. Contrastingly, the bpa complexes do not exhibit emission in fluid solution but give rise to a characteristic higher energy triplet-centered ligand field (^{3}LF) emission in 2-MeTHF at 80 K. When solutions of the $(OC)_5W-L-W(CO)_5$ (L = pyz, bpy, bpe) complexes are cooled to 80 K, the MLCT absorption and emission bands undergo substantial blue shifts and the higher energy ^{3}LF emission is also detected. Emission and excitation data illustrate that at temperatures below the glass transition point the ^{3}LF and ^{3}MLCT excited states are all nonequilibrated.

Introduction

Much attention has been paid to electronic interactions between metal chromophores in ligand-bridged binuclear complexes;[1] on photoexcitation these molecules provide relatively simple models for inner-sphere electron-transfer[2] and intramolecular energy-transfer[3] processes. However, almost all of these studies have been concerned with mixed-valence classical coordination complexes. Currently though, there is substantial interest in the optical[4] and photochemical[5] properties of binuclear zerovalent group 6 metal carbonyl complexes. Reports of ligand-bridged species bound between two $M(CO)_5$ moieties, i.e., $(OC)_5M-L-M'(CO)_5$, and between two $M(CO)_4$ fragments, i.e., $(OC)_4M-L-M'(CO)_4$, (where M, M′ = Cr, Mo, W) have appeared. These studies have illustrated that the binucleating ligand π^*-electron system has a profound effect on the spectroscopic, photochemical, and redox behavior of these complexes. The exceptional solvent sensitivities that are observed in the absorption spectra of a number of these metal complexes have also been rationalized in terms of the electronic characteristics of their bridging ligands.[6]

The $(OC)_5M-L-M'(CO)_5$ (M, M′ = Cr, Mo, W) complexes represent an enormously rich photophysical system as their emission spectra indicate that these molecules are multiple emissive.[5d] Multiple-state emission properties are increasingly being recognized for transition-metal systems,[7] and several metal carbonyl complexes have now been established to exhibit this phenomenon.[8] Known examples include *fac*-$[SRe(CO)_3L]^+$ (S = piperidine, pyridine, CH_3CN, PhCN; L = 1,10-phenanthroline, 2,2′-biquinoline) and *fac*-$XRe(CO)_3L_2$ (X = Cl, Br, I; L = pyridine or a pyridine derivative). These complexes exhibit Re $\rightarrow \pi^*$(L) charge-transfer (CT) and either $\pi \rightarrow \pi^*$ or n $\rightarrow \pi^*$ triplet-centered intraligand (^{3}IL) emissions at 77 K, but the ^{3}IL emission is not observable at room temperature.[9] However, the photophysical properties of the $(OC)_5W-L-W(CO)_5$ molecules are unusual in that the multiple emission spectrum is observed at room temperature. The intent of the present study has therefore

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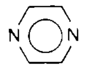
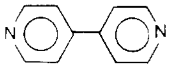
been to identify the excited states involved in this system and to determine the dynamic processes that give rise to the multiple-state emission. The binuclear $(OC)_5W{-}L{-}W(CO)_5$ complexes investigated here are bridged via pyrazine (pyz), 4,4′-bipyridine (bpy), *trans*-1,2-bis(4-pyridyl)ethylene (bpe), and 1,2-bis(4-pyridyl)ethane (bpa) ligands. Emission parameters of the corresponding mononuclear species are also included for comparison.



pyz



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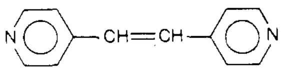

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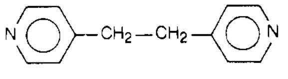

bpa

Experimental Section

Materials and Syntheses. Tungsten hexacarbonyl (Strem) was used as obtained, and the binucleating ligands (Aldrich) were recrystallized prior to use. The mononuclear $(OC)_5WL$ and binuclear $(OC)_5W{-}L{-}W(CO)_5$ complexes were prepared and purified according to a previously described procedure.[5d] Benzene (J. T. Baker) and toluene (Aldrich) used in the spectroscopic measurements were obtained as the best available commercial grades. 2-Methyltetrahydrofuran (2-MeTHF, Aldrich) was purified by refluxing over $LiAlH_4$ according to the procedure described for tetrahydrofuran.[10] Nitrogen gas used for purging was dried and deoxygenated according to a previously reported method.[11]

Equipment and Procedures. UV–visible spectra were recorded on a Hewlett-Packard 8450A microprocessor-controlled diode-array spectrometer, and the reported absorption maxima are considered accurate to ±2 nm. Emission and excitation spectra were obtained on a SLM Instruments Model 8000/8000S spectrometer, which incorporates a photomultiplier-based (Hamamatsu R928) photon-counting detector; the band maxima are believed to be accurate to ±4 nm. In all the emission and excitation experiments the sample solutions were filtered through a 0.22-μm Millipore filter and deoxygenated prior to taking readings. Sample temperatures above 270 K were controlled to ±0.1 K by circulating thermostated water. Emission quantum yields (ϕ_e) were measured relative to $Ru(bpy)_3^{2+}$ in deoxygenated aqueous solution at 283 K as a calibrant (ϕ_e = 0.046)[12] and were corrected for the differing solvent refractive indices, according to a previously published method.[13] The emission quantum yields were reproducible to within ±10%. Emission lifetimes (τ_e) were recorded on a PRA System 3000 time-correlated pulsed single-photon-counting apparatus; this equipment is described in more detail in an earlier paper.[5d] The reported lifetimes at 283 and 80 K were found to be reproducible to within ±5 ns and ±0.5 μs, respectively. Absorption and emission data below 270 K were obtained with an Oxford Instruments DN1704K liquid-N_2-cooled cryostat. Spectral data was recorded from rigorously deaerated solutions contained in a 1-cm path-length quartz cell. The temperature of these solutions was maintained to ±0.2 K by means of an Oxford Instruments Model 3120 controller.

Results

Electronic absorption spectra recorded from ligand-bridged $(OC)_5W{-}L{-}W(CO)_5$ (L = pyz, bpy, bpa) dimers in 2-MeTHF at 295 and 80 K are depicted in Figure 1. Absorption data recorded from the complete series of binuclear $(OC)_5W{-}L{-}W(CO)_5$ and corresponding mononuclear $(OC)_5WL$ complexes in benzene at 295 K and in 2-MeTHF at 80 K are summarized in Table I.

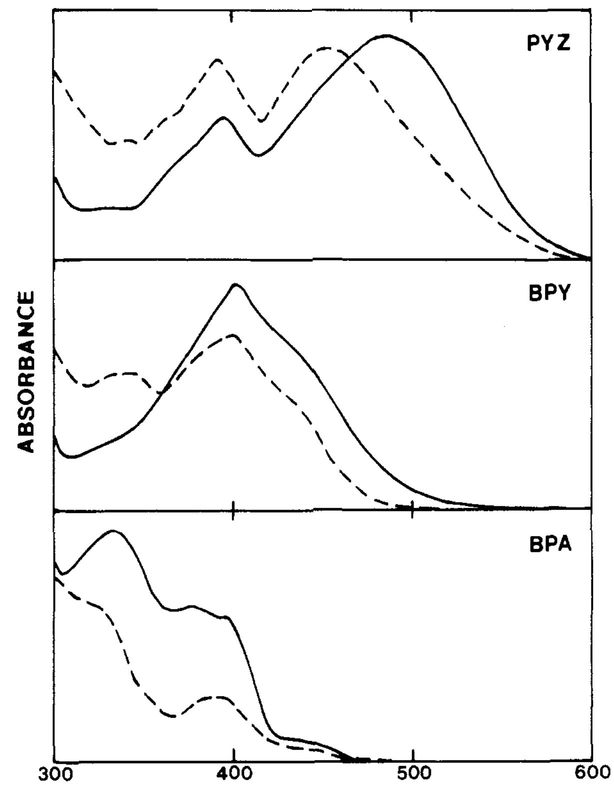

Figure 1. Electronic absorption spectra of $(OC)_5W{-}L{-}W(CO)_5$ (L = pyz, bpy, bpa) complexes in deaerated 2-MeTHF at 295 (—) and 80 K(---).

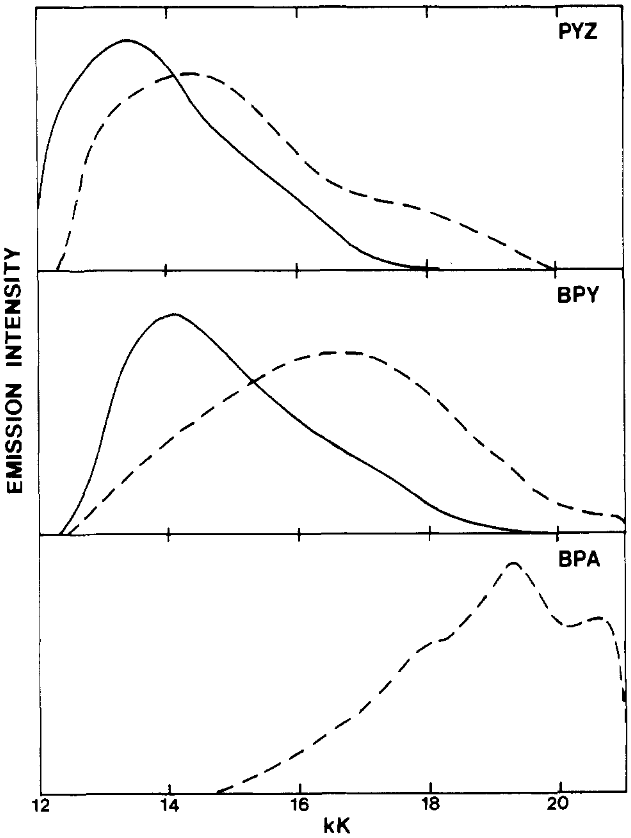

Figure 2. Corrected emission spectra of $(OC)_5W{-}L{-}W(CO)_5$ (L = pyz, bpy, bpa) complexes in deoxygenated toluene at 290 K (—) and in 2-MeTHF at 80 K (- - -). Excitation wavelength is 404 nm for L = pyz and bpy and 380 nm for L = bpa.

Emission spectra observed from $(OC)_5W{-}L{-}W(CO)_5$ (L = pyz, bpy, bpa) complexes in deoxygenated toluene at 290 K and in a 2-MeTHF glass at 80 K are shown in Figure 2. The spectra of $(OC)_5W{-}L{-}W(CO)_5$ (L = pyz, bpy) clearly indicate two low-energy emitting states. Significantly, no emission was observed from $(OC)_5W(bpa)W(CO)_5$ in room temperature solution, and this complex is also distinctive in that its 80 K emission band is at considerably higher energy than the other dimer complexes and it exhibits vibrational structure with $\Delta\nu$ = 1240 cm^{-1}. Likewise, the corresponding mononuclear $(OC)_5W(bpa)$ complex does not emit in room-temperature solution, and it displays a similar

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Table I. Electronic Absorption Spectral Data and Assignments for $(OC)_5W{-}L{-}W(CO)_5$ and $(OC)_5WL$ Complexes at 295 and 80 K[a]

	295 K λ_{max}, nm ($10^4\epsilon$, M^{-1} cm^{-1})		80 K λ_{max}, nm	
complex	$^1A_1 \rightarrow {}^1E$	$M \rightarrow \pi^*(L)$	$^1A_1 \rightarrow {}^1E$	$M \rightarrow \pi^*(L)$
$(OC)_5W(pyz)W(CO)_5$	397 (0.55)	510 (1.20)	390	455
$(OC)_5W(bpy)W(CO)_5$	404 (1.18)	438 (1.08)	356, 398	430 (sh)
$(OC)_5W(bpe)W(CO)_5$	404 (1.47)	450 (1.55)	398	425, 448 (sh)
$(OC)_5W(bpa)W(CO)_5$	379 (1.22)	343 (1.29)	385, 430	318 (sh)
$(OC)_5W(pyz)$	398 (0.71)	*b*	398	*b*
$(OC)_5W(bpy)$	400 (1.03)	*b*	365, 400	*b*
$(OC)_5W(bpe)$	402 (0.36)	440 (sh)	355, 397	424 (sh)
$(OC)_5W(bpa)$	379 (0.30)	340 (sh)	390, 432	*c*

[a] Data at 295 K were recorded in benzene, and data at 80 K were obtained in deaerated 2-MeTHF; sh = shoulder. [b] Overlaps substantially with LF transition. [c] Not observable.

Table II. Corrected Emission Spectral Data for $(OC)_5W{-}L{-}W(CO)_5$ and $(OC)_5WL$ Complexes at 283 and 80 K[a]

	283 K			80 K	
complex	λ_{max}, nm	$10^4\phi_{em}$	τ_e, ns	λ_{max}, nm	τ_e, μs
$(OC)_5W(pyz)W(CO)_5$	721	4.40	186	562 700	1.7, 11.3 8.7
$(OC)_5W(bpy)W(CO)_5$	654	1.59	394	488 596	1.8, 10.2 5.2
$(OC)_5W(bpe)W(CO)_5$	560	0.13	123	464 521	1.6, 9.3 8.9
$(OC)_5W(bpa)W(CO)_5$	*b*			522[c]	1.8
$(OC)_5W(pyz)$	645	0.20	18	580	17.2
$(OC)_5W(bpy)$	643	0.72	415	586	8.9
$(OC)_5W(bpe)$	549	0.10	120	518	11.9
$(OC)_5W(bpa)$	*b*			520[c]	0.18

[a] Data at 283 K were recorded in deoxygenated benzene, and data at 80 K were obtained in deaerated 2-MeTHF. The excitation wavelength was 404 nm, except for bpa complexes where excitation was at 380 nm. Total quantum yields are absolute values and are accurate to within ±10%. Lifetimes at 283 and 80 K are accurate to ±5 ns and 0.5 μs, respectively. [b] No emission was observed. [c] Emission appears as a multiplet (see Figure 2).

low-temperature emission spectrum with $\Delta\nu = 1180$ cm^{-1}. A list of the emission data obtained from all the binuclear and mononuclear complexes studied at 283 and 80 K, including emission quantum yields (ϕ_e) and emission lifetimes (τ_e), is shown in Table II. For each of these complexes, the room-temperature lifetimes of both emission features were found to be identical within the experimental uncertainty, and the observed emission decays were strictly exponential. However, at 80 K the observed lifetimes of the individual emission bands are not equal as listed in Table II. Importantly, none of the emission bands can be attributed to the free ligands because they are not measurably emissive following excitation with the wavelengths employed here.

Figure 3 illustrates the effects that are observed on the emission spectrum of $(OC)_5W(pyz)W(CO)_5$ in deoxygenated toluene when the solution temperature is lowered from 290 to 210 K. There is considerable change in the emission spectral distribution on cooling, with the low-energy band substantially gaining intensity; these changes are most pronounced in the uncorrected spectra. Throughout these temperature changes the emission spectra retain an isoemissive point at 14.05×10^3 cm^{-1}. Emission lifetimes determined at any wavelength under the emission band of these complexes in 210–290 K fluid solution were found to be identical (within experimental error) for each individual complex. The emission spectrum recorded from $(OC)_5W(pyz)W(CO)_5$ in a 2-MeTHF glass at 80 K indicates a substantially different emission spectral distribution (see Figure 3).

Figure 4 shows the effects on the emission spectral distribution of $(OC)_5W(pyz)W(CO)_5$ in 2-MeTHF at 80 K caused by varying the excitation wavelength between 380 and 430 nm. In contrast, emission spectra obtained from each of the complexes at temperatures greater than 200 K (above the glass thawing point) did not exhibit any excitation wavelength dependence over the 320–450-nm range. Excitation spectra of $(OC)_5W(pyz)W(CO)_5$ in a 2-MeTHF glass at 80 K were recorded while the emission was monitored at the two low-energy emission bands, and these are shown in Figure 5. Excitation spectral results obtained from all of the $(OC)_5W{-}L{-}W(CO)_5$ and $(OC)_5WL$ complexes are summarized in Table III.

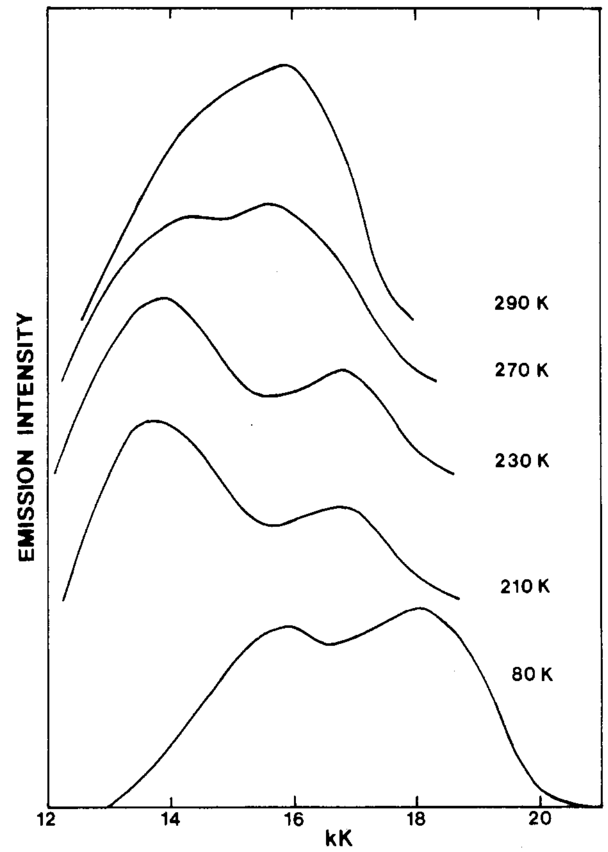

Figure 3. Uncorrected emission spectra of $(OC)_5W(pyz)W(CO)_5$ in deoxygenated toluene at 210–290 K and in a 2-MeTHF glass at 80 K. Excitation wavelength is 404 nm.

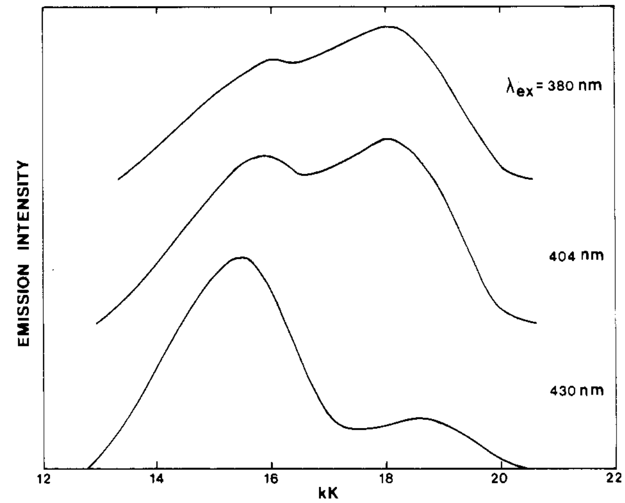

Figure 4. Uncorrected emission spectra of $(OC)_5W(pyz)W(CO)_5$ in 2-MeTHF at 80 K following excitation at (a) 380, (b) 404, and (c) 430 nm.

Discussion

Previously, the room-temperature electronic absorption features of the binuclear $(OC)_5W{-}L{-}W(CO)_5$ system and its corresponding mononuclear $(OC)_5WL$ derivatives have been studied in detail.[4e,5d] The lowest lying absorption bands of these complexes are comprised of ligand (LF) $^1A_1(e^4b_2{}^2) \rightarrow {}^1E(e^3b_2{}^2a_1{}^1)$ and $W(d\pi) \rightarrow (\pi^*)L$ charge-transfer (MLCT) transitions, and the latter absorptions have been noted to be exceptionally solvent sensitive.[6a,e]

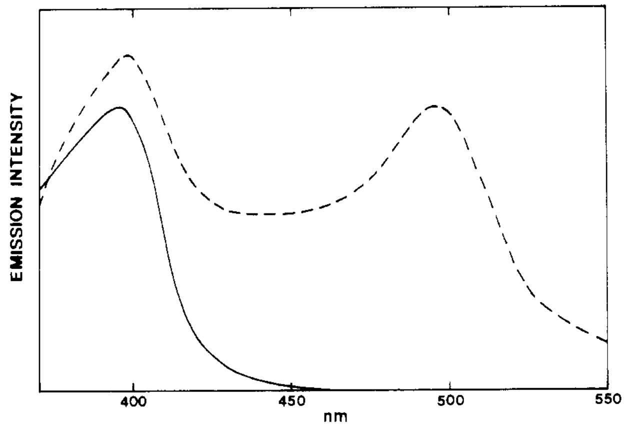

Figure 5. Corrected excitation spectra of $(OC)_5W(pyz)W(CO)_5$ in 2-MeTHF at 80 K. Emission monitored at the 560- (—) and 670-nm (- - -) uncorrected emission maxima.

Table III. Corrected Excitation Spectral Data for $(OC)_5W$-L-$W(CO)_5$ and $(OC)_5WL$ Complexes in 2-MeTHF at 80 K[a,b]

complex	λ_{max}, nm
$(OC)_5W(pyz)W(CO)_5$	397, 494
$(OC)_5W(bpy)W(CO)_5$	358, 398, 428 (sh)
$(OC)_5W(bpe)W(CO)_5$	400, 448
$(OC)_5W(bpa)W(CO)_5$	354, 402, 424 (sh)
$(OC)_5W(pyz)$	360, 402
$(OC)_5W(bpy)$	356, 398
$(OC)_5W(bpe)$	362, 422
$(OC)_5W(bpa)$	358, 410, 424 (sh)

[a] Data recorded in deaerated solutions; sh = shoulder. [b] Emission monitored at uncorrected emission maxima.

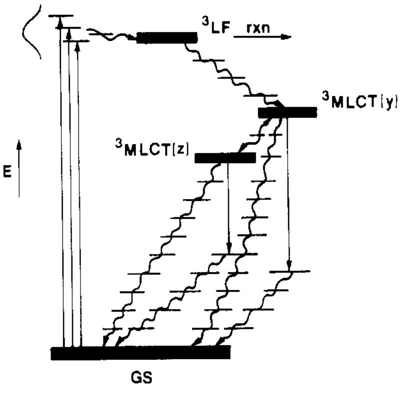

Figure 6. Photophysical scheme for the lowest lying ^{3}LF and ^{3}MLCT excited states of $(OC)_5W$-L-$W(CO)_5$ complexes in fluid solution. Heavy horizontal lines depict the ^{3}LF and ^{3}MLCT states, and light horizontal lines represent successive complex–solvent cage energies as vibrationally excited states relax (only a few of these lines are shown). Vertical and wavy lines denote radiative and nonradiative processes, respectively. The ^{3}MLCT(y) and ^{3}MLCT(z) states are shown to be thermally equilibrated. Reaction from the ^{3}LF system involves W–N bond dissociation.

The W(dπ) → (π*)CO transitions in these molecules appear at wavelengths below 300 nm. A detailed investigation of electronic absorption, photophysical, photochemical, and redox properties of these complexes has illustrated that the ligand π*-acceptor orbitals may be substantially perturbed on binucleation and that the extent of this orbital stabilization relates to the length and conjugation of the binucleating ligand. In earlier work it has been concluded that when L = pyz, bpy, and bpe, the MLCT states are at lowest energy, but when L = bpa, the LF states are lowest lying.[4c,5d]

The low-temperature electronic absorption and emission data presented here reveal a significant environment effect and provide further evidence for the above electronic assignments. The absorption spectra of the pyz, bpy and bpe dimeric complexes, when cooled from fluid solution to 80 K, exhibit a blue shift in the lowest energy MLCT absorption features (see Figure 1 and Table I). This effect is thought to be predominantly a solvent one, produced by the reorientation of the solvent dipoles around the metal complex on changing from a dynamic to a more rigid medium. The environment effect is greater for the binuclear compounds than their corresponding mononuclear derivatives, and it is most pronounced for the ligand-bridged $(OC)_5W(pyz)W(CO)_5$ species; this is in accordance with the earlier solvent interpretation based on specific solvent–solute and induced dipolar interactions.[6e] In contrast, the energies of the LF transitions of these complexes are relatively unaffected by the temperature reduction to 80 K and the accompanying change in the environment (see Figure 1 and Table I). Consequently, the lowest absorption energy features of the $(OC)_5W(bpa)W(CO)_5$ complex are virtually unshifted on cooling from 295 to 80 K (see Figure 1), confirming the LF assignment.

The mononuclear and binuclear complexes, where L = pyz, bpy and bpe, give rise to emission in both 290 and 80 K deoxygenated solutions, in accordance with their MLCT assignments (see Table II). The room-temperature lifetimes range from 18 to 415 ns, which are fairly typical of triplet-centered emissions from MLCT states of metal carbonyl complexes in fluid solution.[5d,8] When the solutions of the complexes are cooled to 80 K, these emission bands significantly blue shift (see Figure 2), an effect previously referred to as "luminescence rigidochromism"[9a,14] and one recognized for other metal carbonyl MLCT systems.[8] Again, this phenomenon is believed to relate to the dramatic change in the local solvent environment that occurs about the metal complex when the solution freezes. Importantly, the emission spectra of $(OC)_5W$-L-$W(CO)_5$ (L = pyz, bpy) clearly indicate the presence of a second radiative state (see Figure 2). In earlier work these transitions have been characterized to be y- and z-polarized orbitally allowed ^{3}MLCT transitions that originate from the metal d(b_{1g}) and d(b_{2g}) orbitals, respectively.[4c,5d] Hereafter, these transitions will be referred to as the ^{3}MLCT(y) and ^{3}MLCT(z) components; the ^{3}MLCT(y) emission component has been shown to be the higher energy one. Significantly, the identical lifetimes of these ^{3}MLCT(y) and ^{3}MLCT(z) components illustrate that these states are in thermal equilibrium under fluid solution conditions. At 80 K, though, the system is no longer thermally equilibrated as the emission lifetimes of the two MLCT excited states are not equivalent (vide infra).

The emission results obtained from the $(OC)_5W(bpa)W(CO)_5$ and $(OC)_5W(bpa)$ complexes are quite different from those for the other molecules, and they support the previously made ^{3}LF assignment.[5d] First, the ^{3}LF emission is only detectable at low temperature in the rigid glass (see Figure 2 and Table II), consistent with the efficient ^{3}LF solution photoreactivity of these bpa molecules.[5d] Second, the emission is at much higher energy than the ^{3}MLCT components of the pyz, bpy, and bpe complexes. Third, the emission lifetimes are appreciably shorter than the values for the ^{3}MLCT emission decays. It is also noted that the 80 K emission spectra of both bpa complexes are distinctive in that they exhibit vibrational structure; the spacing is $\Delta\nu$ = 1240 cm^{-1} for $(OC)_5W(bpa)W(CO)_5$ and $\Delta\nu$ = 1180 cm^{-1} for $(OC)_5W(bpa)$. This progression is thought to relate to the ν(C–C) or δ(C–H) ground-state vibrational modes on the $-CH_2-CH_2-$ linkage between the pyridyl rings of the bpa ligand.

Temperature and excitation wavelength effects on the emission spectra obtained under fluid conditions shed light on the nature of the dynamic photophysical processes of the binuclear $(OC)_5W$-L-$W(CO)_5$ molecules. The observed emission data clearly reflect an excited-state system that is thermally equilibrated at temperatures above the 2-MeTHF glass melting point: between 210 and 290 K there is no observable excitation wavelength dependence on the emission spectra, and the recorded lifetimes are coincident at any wavelength under the multiple emission band envelope. A Boltzmann model, in which the ^{3}MLCT(y) and ^{3}MLCT(z) excited states are rapidly interconverting, is adopted

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[14] Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998.

to account for the emission behavior (see Figure 6). In this scheme the rate of interconversion between the two ^{3}MLCT excited states is more rapid than the rates of radiative or nonradiative deactivation from the individual ^{3}MLCT levels. The observed temperature dependence of the emission spectra of $(OC)_5W(pyz)W(CO)_5$ shown in Figure 3 has been fitted to the modified Boltzmann expression (eq 1).[7d,h,15] Here, I_u and I_l are the emission

$$\frac{I_u}{I_l} = \frac{g_u k_u}{g_l k_l}\exp\left(\frac{-\Delta E}{k_B T}\right) \qquad (1)$$

intensities of the upper (u) and lower (l) MLCT levels measured at 16.80×10^3 and 13.75×10^3 cm^{-1}, respectively, k_u and k_l denote the radiative rate constants from these excited states, g is a degeneracy factor, ΔE represents the energy gap between the emitting levels, k_B is the Boltzmann constant, and T is temperature.[16] A least-squares analysis of the data in Figure 3 yields $\Delta E = 370$ ($\pm$85) cm^{-1} and $g_u k_u / g_l k_l = 6.2$. Although these results are the first of their kind obtained from a metal carbonyl system, they are in good agreement with those for other classical coordination complexes that are thermally equilibrated in fluid solution.[7a,d,h] Importantly, the ΔE value, being within a recognized equilibrium limit of $\sim$1000 cm^{-1},[15a] is sufficiently small to rationalize the rapid thermal back-population.

When the solution temperature is further cooled to 80 K the observed emission spectrum takes on a very different distribution (see Figure 3). Two factors apparently give rise to this spectral change. The first one is that the MLCT transitions on cooling through the glass transition point display significant "luminescence rigidochromism", as alluded to above, and these bands both blue shift substantially. The second effect is that at 80 K the upper energy MLCT(y) emission gains considerable intensity from the now radiating ^{3}LF state, and the latter feature consequently dominates the high-energy side of the spectrum. Emission lifetimes and excitation spectra obtained from the complexes at 80 K also support this MLCT/LF interpretation (vide infra).

Not surprisingly, the dynamics of excited-state interconversion are much altered at 80 K. It appears that the thermal equilibrium between the ^{3}MLCT(y) and ^{3}MLCT(z) states is now lost and, indeed, all three MLCT/LF levels are nonequilibrated. This conclusion is supported by the lifetimes obtained at 80 K, which are different for each ^{3}MLCT emission band and further indicate the participation of the ^{3}LF levels (see Table II). The striking excitation wavelength dependence on the emission spectral distribution (see Figure 4) also confirms the lack of a thermal equilibrium in the frozen solutions. Excitation spectra obtained from complexes at 80 K (see Table III) indicate maxima corresponding to the MLCT and LF absorptions and are consistent with the nonequilibrated model of excited-state decay. This is illustrated by the excitation spectra of $(OC)_5W(pyz)W(CO)_5$, which are strongly dependent on the choice of the monitoring emission wavelength (see Figure 5). When the emission is recorded at 670 nm two excitation features are observed; the 494-nm band is attributed to the ^{3}MLCT manifold, and the 397-nm band indicates that the ^{3}LF state effectively nonradiatively populates the ^{3}MLCT emitting levels. When the emission is observed at 560 nm, the ^{3}LF state clearly dominates the excitation spectrum as it undergoes direct radiative decay to the ground state.

Conclusions

The temperature dependence and excitation wavelength dependence of the emission from $(OC)_5W{-}L{-}W(CO)_5$ (L = pyz, bpy, bpe) complexes in fluid solution may be understood in terms of two thermally equilibrated ^{3}MLCT excited states separated by approximately 370 cm^{-1}. When the solution is cooled through the glass transition point the MLCT levels become non-equilibrated and their absorption and emission bands undergo substantial energy shifts. A third ^{3}LF emission component is also observable from the glass solutions at low temperature.

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Registry No. $(OC)_5W(pyz)W(CO)_5$, 70738-71-5; $(OC)_5W(bpy)W(CO)_5$, 81178-10-1; $(OC)_5W(bpe)W(CO)_5$, 81178-12-3; $(OC)_5W(bpa)W(CO)_5$, 81178-11-2; $(OC)_5W(pyz)$, 65761-19-5; $(OC)_5W(bpy)$, 81178-09-8; $(OC)_5W(bpe)$, 113110-66-0; $(OC)_5W(bpa)$, 113110-67-1.

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(16) Quantum yields were not used in these calculations because the corrected emission spectra (see Figure 2) could not be adequately deconvoluted.

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Knudsen Effusion Mass Spectrometric Investigation of Palladium–Germanium Clusters

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The equilibria involving the gaseous species Pd, PdGe, $PdGe_2$, and $PdGe_3$ above the condensed system Pd–Ge have been investigated by means of the Knudsen effusion mass spectrometric technique at temperatures between 1694 and 1946 K. The equilibrium constants, K_p, for the various reactions were evaluated, and the respective reaction enthalpies were determined. By combination of these reaction enthalpies with the appropriate ancillary data, the atomization energies ($\Delta H_a{}^\circ{}_0$) and standard heats of formation ($\Delta H_f{}^\circ{}_{298}$), in kJ mol^{-1}, were obtained for $PdGe_2(g)$ and $PdGe_3(g)$, respectively, and are as follows: 600 ± 25, 516 ± 25; 989 ± 40, 503 ± 40.

Introduction

Investigations into the physical and chemical properties of small atomic and molecular aggregates, particularly metal clusters, are of considerable current interest.[1-3] Most experimental bond energies of diatomic metals and small metal clusters have been measured by Knudsen effusion mass spectrometry and have been summarized in several reviews.[4-6]

The present investigation has been performed as part of our research program aimed at the determination of thermodynamic

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