Experimental Section

$^{57}Fe_2O_3$ (16.2 mg, 0.100 mmol) was heated to 50 °C in concentrated hydrochloric acid (5 mL) for 1 h or until there was no trace of solid Fe_2O_3. The hydrochloric acid was evaporated in vacuo to near dryness. Chlorobenzene (100 mL, freshly distilled from CaH_2) was added to the aqueous ferric chloride, and the mixture was heated to reflux under argon. About 50 mL of the solvent was distilled off in order to remove the remaining water as an azeotrope. The color of the suspension shifted from pale yellow to dark brown as the anhydrous iron was reduced.[9] The temperature was then allowed to drop to 70 °C. The porphyrin (0.118 mmol) was dissolved in chlorobenzene (4 mL, freshly distilled from CaH_2) and 2,4,6-trimethylpyridine (0.15 mL) was added. The solution was degassed by three freeze–pump–thaw cycles and transferred to the ferrous chloride suspension via a gastight syringe. The atmosphere in the reaction flask was carefully kept free from oxygen.

The reaction was followed by measurement of the electronic absorption spectra of aliquots of the solution. After 4–16 h, the insertion was complete and the solvent was evaporated. The residue was dissolved in toluene (50 mL) and extracted with several portions of water to remove the excess of iron, which can thus be recycled. The porphyrin solution was then washed with hydrochloric acid (4 × 15 mL, 0.2 M) and water (2 × 20 mL). The organic layer was dried over Na_2SO_4, and the solvent was evaporated. The iron(III) porphyrin chloride was recrystallized from CH_2Cl_2/hexane, and a typical yield was 0.112 mmol (95%). It is easily identified by the electronic absorption spectrum in the visible region and the ^1H NMR spectrum, which shows large, positive paramagnetic shifts.[3]

Registry No. $^{57}Fe_2O_3$, 64886-55-1; HCl, 7647-01-0; $^{57}FeCl_3$, 120028-37-7; $^{57}FeCl_2$, 75297-20-0; ^{57}Fe(tetraphenylporphyrin), 124419-55-2; ^{57}Fe[α,α,α-*meso*-tetrakis(*o*-pivalamidophenyl)porphyrin], 124419-56-3; ^{57}Fe[α-5,15-(2,2′-(nonanediamido)diphenyl)-α,α-10,20-bis(*o*-pivalamidophenyl)porphyrin], 124419-57-4; ^{57}Fe[α-5,15-(2,2′-(decanediamido)diphenyl)-α,α-10,20-bis(*o*-pivalamidophenyl)porphyrin], 124419-58-5; ^{57}Fe[α-5,15-(2,2′-(dodecanediamido)diphenyl)-α,α-10,20-bis(*o*-pivalamidophenyl)porphyrin], 124419-59-6.

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Electronic Energy Transfer from Zerovalent Binuclear Tungsten Carbonyl Complexes to Organic Triplet States

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There has been substantial interest in the mechanism of electron-, charge-, and energy-transfer reactions of coordination complexes.[1,2] Lately, much attention has been paid to optically induced energy and electron transfer between transition-metal chromophores that are covalently linked in a supermolecular structure.[3] Intramolecular mechanisms of mixed-valence dimer and trimer complexes have been extensively studied.[4]

The most systematic investigations to date, however, have been concerned with the quenching of organic triplet states by a series of Cr(III) complexes.[5] Notably, even though all of the acceptors have lowest energy excited states (^2E_g) considerably below the donor energy levels ($^3D^*$), the obtained quenching rate constants (k_q) are abnormally low and differ substantially over the range of complexes. A general classical treatment of vertical and nonvertical energy transfer has been applied by Balzani et al. to explain this nonadiabatic behavior, and these authors have concluded that the preexponential factor of the energy-transfer rate constant is the rate-determining parameter in the exothermic energy-transfer mechanism.[6] This classical approach to energy transfer is analogous to the treatment of outer-sphere electron-transfer reactions.[6,7] In related work, Wilkinson et al. have illustrated that these lower transmission coefficients for collisional energy transfer are, in part, due to steric effects of the ligand substituent groups in these Cr(III) complexes[5b,8] and in other metal complex acceptors.[9]

Most investigations at this time have involved organic triplet states as energy donors, and relatively few have been concerned with energy-transfer mechanisms for inorganic molecules as the energy donors.[10] In particular, detailed quenching studies of transition-metal organometallic complexes as energy donors have not previously appeared. A number of metal carbonyl complexes have now been established to luminesce in room-temperature hydrocarbon solution, and although the radiative routes are invariably thought to originate from metal-to-ligand charge-transfer excited states,[11] the precise energy positions of these emitting levels have rarely been determined. Moreover, the opportunity now exists to explore energy transfer from low-valent organometallic molecules to organic triplet states. In this paper we report the results of such a study for the ligand-bridged zerovalent $(OC)_5W(bpy)W(CO)_5$ (bpy = 4,4′-bipyridine) complex.

Experimental Section

Materials and Synthesis. Starting material tungsten hexacarbonyl was obtained from Strem Chemical Co. and used without further purification. The ligand 4,4′-bipyridine (bpy) was obtained from Aldrich Chemical Co. and recrystallized prior to use. Quenchers employed were all purchased from Aldrich Chemical Co. and purified by vacuum sublimation or distillation under N_2, as appropriate. Benzene used as solvent in the photophysical measurements was obtained from J. T. Baker Chemical Co. as Photrex grade. All other chemicals and solvents used in the synthesis of $(OC)_5W(bpy)W(CO)_5$ were of reagent grade. Nitrogen used for purging samples was rigorously deoxygenated and dried according to a reported procedure.[12] The complex $(OC)_5W(bpy)W(CO)_5$ was prepared and purified as described previously.[13]

Equipment and Procedures. Absorption spectra were recorded on a Hewlett-Packard 8450A spectrometer, which utilizes a microprocessor-controlled diode-array detector. In the emission experiments the sample

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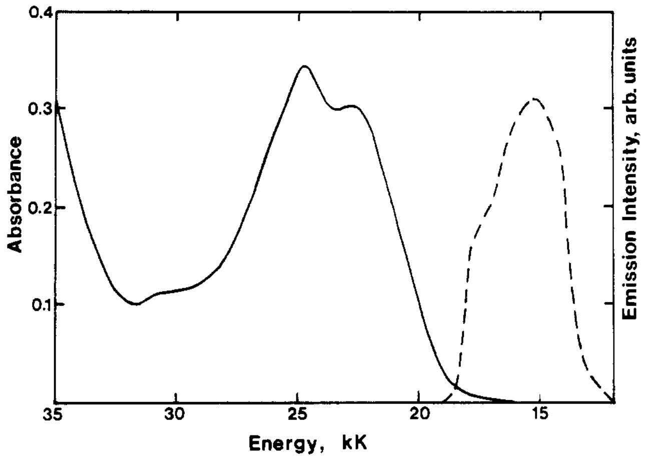

Figure 1. Absorption (—) and emission (- - -) spectra for $(OC)_5W(bpy)W(CO)_5$ in deoxygenated benzene at 283 K. The emission spectrum is fully corrected and was recorded following excitation at 404 nm.

solutions were deoxygenated by N_2 purging for 15 min and filtered through a 0.22-μm Millipore filter prior to measurement; the solution temperature was controlled to ±0.1 K. Emission spectra were recorded on a SLM Instruments Model 8000/8000S spectrometer incorporating a photomultiplier-based photon-counting detector. The emission quantum yield (ϕ_e) of $(OC)_5W(bpy)W(CO)_5$ was determined by using the Parker–Rees method with dilute $Ru(bpy)_3^{2+}$ in deoxygenated aqueous solution at 283 K as a calibrant ($\phi_e = 0.046$).[14] The determined value was corrected for the differing refractive indices of the solvents[15] and found to be reproducible to ±10%. Emission lifetimes were measured on a PRA Model 3000 time-correlated pulsed single-photon-counting system.[16] Samples were excited with light from a PRA Model 510 nitrogen flash lamp that was transmitted through an Instruments SA Inc. H-10 monochromator. Emission light was detected from the sample at 90° by means of a second H-10 monochromator and a thermoelectrically cooled red-sensitive Hamamatsu R955 photomultiplier tube. Resulting photon counts were stored on a Tracor Northern Model 7200 microprocessor-based multichannel analyzer; each set of data were typically acquired over a 12-h period. The instrument response function was subsequently deconvoluted from the emission data to obtain an undisturbed decay curve that was fitted by using a least-squares procedure on an IBM PC. Each sample exhibited single-exponential decays, and the lifetimes (recorded in triplicate) were observed to be reproducible to within ±5 ns.

In the energy-transfer experiments all samples were excited at the absorption maximum (404 nm) and observed at the emission maximum (608 nm) of the $(OC)_5W(bpy)W(CO)_5$ complex. During these measurements it was ensured that the quenchers neither absorbed nor emitted significantly at these wavelengths. Typically, the absorbance of $(OC)_5W(bpy)W(CO)_5$ at 404 nm was 0.4–0.6; the molar absorptivity of this complex in 283 K benzene at 404 nm is 11 800 M^{-1} cm^{-1}.

Results

Electronic absorption and emission spectra recorded from $(OC)_5W(bpy)W(CO)_5$ in deoxygenated benzene at 283 K are depicted in Figure 1. Although the emission spectrum exhibits band structure, the spectral distribution was observed to be independent of excitation wavelengths greater than 300 nm. Additionally, a single lifetime was observed from the $(OC)_5W(bpy)W(CO)_5$ complex and this was constant at any wavelength throughout the emission band. The emission quantum yield (ϕ_e) and the lifetime (τ_e) for this complex in deoxygenated benzene at 283 K were determined to be 1.59×10^{-4} and 394 ns, respectively. Radiative (k_r) and nonradiative (k_{nr}) decay constants have been derived from the experimentally observed parameters with eq 1 and 2. The calculated values for $(OC)_5W(bpy)W(CO)_5$ in deoxygenated benzene at 283 K are $k_r = 4.0\ (\pm 0.5) \times 10^2\ s^{-1}$ and $k_{nr} = 2.5\ (\pm 0.1) \times 10^6\ s^{-1}$.

$$k_r = \phi_e/\tau_e \tag{1}$$

$$k_{nr} = \frac{1}{\tau_e} - k_r \tag{2}$$

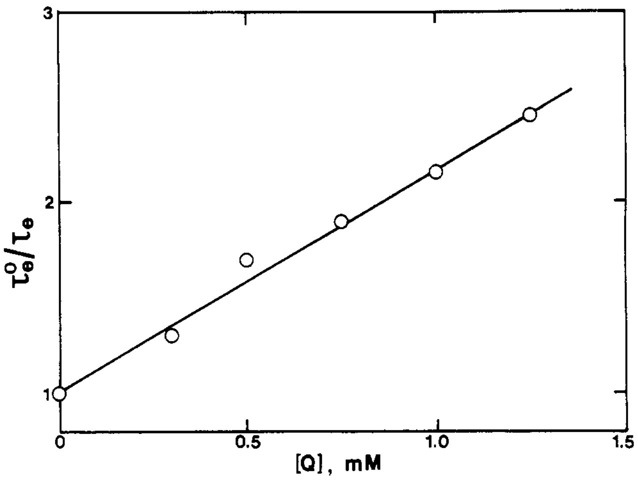

Figure 2. Stern–Volmer plot for quenching of $(OC)_5W(bpy)W(CO)_5$ by biacetyl (E_T = 19 700 cm^{-1}) in deoxygenated benzene at 283 K.

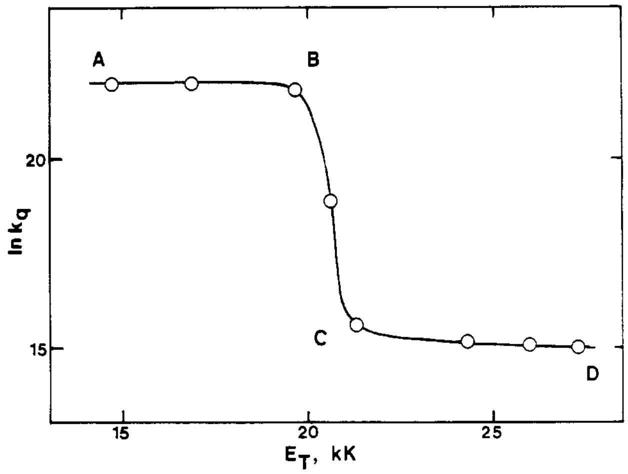

Figure 3. Dependence of ln k_q vs E_T for energy-transfer quenching of $(OC)_5W(bpy)W(CO)_5$ by various organic triplet quenchers. Data were recorded in deoxygenated benzene solution at 283 K.

Energy-transfer measurements have been performed by using various organic triplet molecules acting as quenchers of the $(OC)_5W(bpy)W(CO)_5$ emission. Emission lifetimes (τ_e) have been obtained at various quencher concentrations, [Q], in deoxygenated benzene solution at 283 K, and the results are summarized in Table I. In the specific case of biacetyl the formation of the quencher triplet state was confirmed by observing its known emission spectrum following excitation exclusively into the $(OC)_5W(bpy)W(CO)_5$ donor. Bimolecular Stern–Volmer quenching constants (k_q) have been determined according to eq 3, where τ_e°

$$\tau_e^{\circ}/\tau_e = 1 + k_q\tau_e^{\circ}[Q] \tag{3}$$

and τ_e are the emission lifetimes in the absence of added quencher and at varying [Q], respectively. In each case a linear Stern–Volmer plot was obtained and the k_q value was determined from the slope of the graph with a modified least-squares fit at fixed point (0,1):

$$k_q\tau_e^{\circ} = \frac{\sum x_iy_i - \sum x_i}{\sum x_i^2} \tag{4}$$

Here, $\sum x_i$, $\sum x_iy_i$, and $\sum x_i^2$ are the summations over all points on the graph. The Stern–Volmer plot for biacetyl as quencher is representative of the series, and it is shown in Figure 2; the calculated k_q values for each of the quenchers are listed in Table I. For the molecules anthracene (E_T = 14 700 cm^{-1}), pyrene (E_T = 16 850 cm^{-1}), and biacetyl (E_T = 19 700 cm^{-1}) efficient emission quenching was observed as reflected by the k_q values in the range

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Table I. Data for Energy-Transfer Quenching of $(OC)_5W(bpy)W(CO)_5$ by Organic Triplets[a,b]

quencher, Q	E_T,[c] cm^{-1}	[Q], M	τ_e, ns	k_q, M^{-1} s^{-1}
anthracene	14700	0.0005	228	3.7×10^9
		0.001	158	
		0.002	101	
pyrene	16850	0.00025	290	3.6×10^9
		0.0005	229	
		0.00075	192	
		0.001	165	
biacetyl	19700	0.00025	304	3.0×10^9
		0.0005	231	
		0.00075	207	
		0.001	183	
		0.00125	161	
p-terphenyl	20600	0.002	338	1.5×10^8
		0.005	287	
		0.01	252	
naphthalene	21300	0.01	388	6.2×10^6
		0.05	365	
		0.1	333	
		0.15	304	
		0.2	251	
benzophenone	24300	0.2	292	3.9×10^6
		0.3	266	
		0.4	247	
		0.5	228	
acetophenone	25950	0.2	304	3.7×10^6
		0.4	248	
		0.5	224	
		0.75	190	
acetone	27273	0.2	312	3.4×10^6
		0.3	279	
		0.4	255	
		0.5	238	

[a] Data recorded in deoxygenated benzene at 283 K. Emission lifetime in absence of quencher is 394 ns. [b] Excitation wavelength is 404 nm; emission lifetimes measured at 608 nm. [c] Values obtained from: Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970. Wilkinson, F. *Organic Molecular Photophysics*; Birks, J., Ed.; Wiley: New York, 1975.

$3-4 \times 10^9$ M^{-1} s^{-1}. For *p*-terphenyl (E_T = 20600 cm^{-1}) the quenching efficiency is reduced, as illustrated by the k_q value of 1.6×10^8 M^{-1} s^{-1}. For naphthalene (E_T = 21300 cm^{-1}), benzophenone (E_T = 24300 cm^{-1}), acetophenone (E_T = 25950 cm^{-1}), and acetone (E_T = 27273 cm^{-1}) the energy-transfer efficiencies were decreased considerably (k_q values are in the range $3-7 \times 10^6$ M^{-1} s^{-1}) and quenching was only observed at high [Q]. The dependence of bimolecular energy-transfer quenching of $(OC)_5W(bpy)W(CO)_5$ by the series of organic triplets is represented in Figure 3 by a plot of ln k_q vs E_T. From the inflection point of this graph we estimate the energy of the lowest lying excited-state manifold of $(OC)_5W(bpy)W(CO)_5$ to be 20300 (±400) cm^{-1}. In all the emission experiments the band maximum was unshifted on addition of quencher and there was no indication of any spectral interference from exciplex or molecular complex formation. Furthermore, the degree of $(OC)_5W(bpy)W(CO)_5$ photodissociation in the course of these measurements was determined to be negligible.

Discussion

1. Nature of the Luminescence. The electronic characteristics of the lowest energy excited states and the photophysical behavior of the $(OC)_5W(bpy)W(CO)_5$ complex have recently been studied in detail.[13,17] Briefly, the emission arises from two close-lying $W(d\pi) \rightarrow \pi^*(bpy)$ metal-to-ligand charge-transfer (MLCT) states that are thermally equilibrated in fluid solution. Consequently, variations in the excitation wavelength do not affect the emission spectral distribution and in each case the emission decays were fitted to a single exponential with a lifetime value constant at any wavelength under the emission band. In addition, the calculated k_r and k_{nr} values, and the relatively long-lived nature of these excited states compared to most organometallic complexes in fluid solution,[11] indicate that these MLCT emission bands are predominantly from triplet levels. Detailed studies of the spin character of the emission including the effects of varying the metals for a range of $(OC)_5M-L-M'(CO)_5$ (M, M' = Cr, Mo, W) complexes have also been reported earlier.[13,17]

2. Energy-Transfer Mechanisms. Figure 3 exhibits upper and lower plateaus and a region where k_q changes substantially; the mechanism of energy transfer in these regions is discussed below.

A–B Plateau, Where $E_T{}^D > E_T{}^A$. In this region exothermic exchange energy-transfer mechanisms dominate as the observed bimolecular rate constants ($(3-4) \times 10^9$ M^{-1} s^{-1}) approach the diffusion limit:

$$k_q \approx k_{diff} = \frac{8RT}{3000\eta}\ (M^{-1}\ s^{-1}) \tag{5}$$

Here, k_{diff} is the diffusion-controlled rate constant, R is the gas constant, and η is the solvent viscosity at temperature T.[18] The diffusion limit calculated for bimolecular exchange in benzene solvent at 283 K is 8.3×10^9 M^{-1} s^{-1}, and so the observed k_q values in this upper plateau are only just below the expected range. In the A–B region the energy-transfer process is expected to be irreversible, as represented by eq 6 and 7.

$$D^* + A \underset{k_{-q}}{\overset{k_q}{\rightleftharpoons}} D + A^* \tag{6}$$

$$k_q[D^*][A] \gg k_{-q}[D][A^*] \tag{7}$$

The slightly lower than expected k_q values may be attributed to steric hindrance between the donor and acceptor molecules; this will reduce the rate of bimolecular energy transfer because of ineffective orbital overlap of the appropriate wave functions.[19] In this context we have recently shown that Franck–Condon perturbations of the MLCT excited states of a series of these $(OC)_5W-L-W(CO)_5$ complexes are substantial[13,17] and this may contribute to a reduction in the orbital interactions, and hence, the k_q values.[6] For the binuclear $(OC)_5W(bpy)W(CO)_5$ molecule this Franck–Condon reorganization energy is thought to involve twisting about the pyridyl rings.[13,17]

A slight decrease in k_q value is noted on replacing the anthracene or pyrene quenchers by biacetyl (see Table I). This is primarily attributed to the onset of efficient reversible exchange processes as $E_T{}^A$ approaches $E_T{}^D$; previously it has been demonstrated that these mechanisms become important as $\Delta E_T <$ 1400–1800 cm^{-1}, where $\Delta E_T = E_T{}^D - E_T{}^A$ or $E_T{}^A - E_T{}^D$.[18]

B–C Region, Where $E_T{}^D \approx E_T{}^A$. In this region the net rate of energy transfer is less than the diffusion-controlled limit. This is attributed to contributions from reversible energy-transfer mechanisms and is represented by eq 6 and an equilibrium constant K, shown in eq 8. Here, the acceptor's energy ($E_T{}^A$) is within the reversible limit of 1400–1800 cm^{-1} from that of the donor's energy ($E_T{}^D$) previously shown for other systems.[18c,e] Recently, the relationship between the equilibrium constant (K) and the standard free energy change (ΔG) accompanying the energy-transfer step has been explored in detail.[2b,6] According to a general treatment presented by Balzani et al. based on a series of Cr(III)

$$K = \frac{k_q}{k_{-q}} = \frac{[D][A^*]}{[D^*][A]} \tag{8}$$

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complexes, the reduced quenching ability may be associated with a lower transmission coefficient for energy transfer. In our study the sharp decline in k_q is in accordance with this interpretation, and this is reflected by the value of $k_q = 1.6 \times 10^8$ M^{-1} s^{-1} for the *p*-terphenyl quencher as the $E_T{}^A$ energy of 20600 cm^{-1} is close to the estimated $E_T{}^D$ energy of 20300 (±400) cm^{-1}.

The sharp drop of k_q in this region can also be rationalized by consideration of eq 9, as detailed by Balzani and his co-workers,[6]

$$k_q = \frac{k_d}{1 + e^{\Delta G/RT} + \dfrac{k_{-d}}{k_{en}{}^{\circ}}(e^{\Delta G^*/RT})} \qquad (9)$$

where ΔG^* and ΔG are the free energy of activation and the standard free energy change of the forward energy-transfer step, respectively, k_d is the diffusion-controlled rate constant, and k_{en} is the transmission coefficient. This expression provides a unified view of the so-called "vertical and nonvertical" energy-transfer behavior. It gives a better explanation or understanding for the slight lowering of k_q values of the energy-transfer processes in the endo- or exoergonic regions. The low values of k_q exhibited in this region cannot be attributed to an activation energy term because no such energy is anticipated for isoergonic energy transfer between excited states. Furthermore, low values of the preexponential factor ($k_{en}{}^{\circ}$) arising from "poor" overlap between the donor and acceptor orbitals may lead to reduced k_q values. The $k_{en}{}^{\circ}$ is a function of the electronic interaction energy between initial and final states, which has the form of an exchange integral between donor and acceptor orbitals. As stated above, the exchange energy transfer requires favorable and simultaneous overlap of two orbital pairs in the donor-acceptor couple. Therefore, in our case the reduction in orbital interaction must arise from steric factors and/or the Franck-Condon distortion effects noted above.

C-D Plateau, Where $E_T{}^D < E_T{}^A$. In this region quenching is only observed at high [Q]. The energy-transfer processes are expected to be inefficient in this region (even if they are spin-allowed) because there is no overlap of the absorption spectra and, thus, no energy matching. Hence, in theory energy transfer should not take place because the overlap integral of the common electronic states is zero.

The presence of the lower plateau indicates that if energy transfer is occurring, it does not proceed by a simple collisional mechanism from the ^{3}MLCT excited state, as eq 9 predicts an exponential decrease in k_q as the energy gap between the donor and acceptor is increased. Considering a coulombic or efficient Forster-type mechanism, it has been shown previously that the rate of energy transfer is also decreased exponentially as the process becomes endothermic according to eq 10,[18e,20] where ΔE_T

$$k_q = k_d \exp(-\Delta E_T/RT) \qquad (10)$$

is a measure of the energy difference between the donor and the acceptor and k_d is the diffusion-controlled rate constant. With use of the obtained $k_d = 3.7 \times 10^9$ M^{-1} s^{-1} and $E_T{}^D = 20300$ cm^{-1} values and the endothermic mechanism (eq 10), the calculated k_q values are for naphthalene $k_q = 2.3 \times 10^7$ M^{-1} s^{-1}, benzophenone $k_q = 3.7$ M^{-1} s^{-1}, acetophenone $k_q = 1.2 \times 10^{-3}$ M^{-1} s^{-1}, and acetone $k_q = 9.2 \times 10^{-6}$ M^{-1} s^{-1}, clearly not consistent with our experimental data.

At the present time no convincing rationale has emerged that provides support for an energy-transfer mechanism in the C-D plateau region. Previously, however, the photophysical properties of $(OC)_5W(bpy)W(CO)_5$ have been shown to be solvent sensitive, whereby emission quantum yields and emission lifetimes are diminished as the solution environment becomes more polar; these effects are predominantly manifested in k_{nr} from the ^{3}MLCT excited state.[17b] Consequently, it is suggested that the lifetime reductions in the C-D plateau region are associated not with energy transfer but with solvation changes; on addition of these ketones to 0.2-0.5 M the solutions have become quite polar. Another possibility is that under these exceptional conditions of high quencher concentration impurity quenching may take place. However, this possibility is not supported by the fact that the lifetimes were not found to vary following different purification methods of the ketone quenchers.

Conclusions

Studies of the emission and emission quenching of $(OC)_5W(bpy)W(CO)_5$ have elucidated the nature of energy transfer from the lowest energy excited states in this ligand-bridged organometallic molecule. The $(OC)_5W(bpy)W(CO)_5$ emission is attributed to two close-lying $W(d\pi) \rightarrow \pi^*(bpy)$ metal-to-ligand charge-transfer (MLCT) excited states centered at 20300 (±400) cm^{-1} that are in thermal equilibrium. Both the photophysical decay parameters and the quenching behavior of this complex are consistent with the MLCT states being primarily of triplet character.

Emission lifetime quenching by a range of organic triplet states reveals that several types of energy-transfer mechanisms can take place. When $E_T{}^D$ is at substantially greater energy than $E_T{}^A$, exothermic exchange processes prevail and the observed bimolecular quenching constant approaches the diffusion-controlled limit. As $E_T{}^A$ approaches (or lies narrowly above) $E_T{}^D$, then reversible energy-transfer mechanisms become influential and the quenching efficiency is greatly diminished. When $E_T{}^A$ lies further above $E_T{}^D$, the lifetime reductions are only observed at high quencher concentrations, and they cannot be rationalized with a simple collisional mechanism involving the quencher molecules.

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Registry No. $(OC)_5W(bpy)W(CO)_5$, 81178-10-1; anthracene, 120-12-7; pyrene, 129-00-0; biacetyl, 431-03-8; *p*-terphenyl, 92-94-4; naphthalene, 91-20-3; benzophenone, 119-61-9; acetophenone, 98-86-2; acetone, 67-64-1.

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Crystal Structure and Magnetic Properties of a Novel Hetero Tetranuclear ZnCuCuZn Complex

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In recent years, there has been great interest in the magnetic properties of the polynuclear transition-metal complexes, especially the polynuclear copper complexes. Much attention has been focused on the magnetostructural correlations and the exchange mechanism, and a large amount of work has been done and reported.[1] However, most study has been on the chloro-, bromo-, sulfido-, and hydroxo-bridged copper complexes, and much less study exists on the structures and magnetic properties of O-R (where R is aromatic ring) bridged parallel-planar copper complexes and none on the correlation between the magnetic and structural characteristics of these complexes.

Recently, we have determined the crystal structure and magnetic properties of binuclear copper complex with picolinaldehyde *N*-oxide thiosemicarbazone.[2] This compound shows a parallel-planar structure, in which two copper(II) ions are linked by the

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