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# Communications

## Direct Observation of Intramolecular Electron Transfer in a Photochemically Prepared Mixed-Valence Dimer

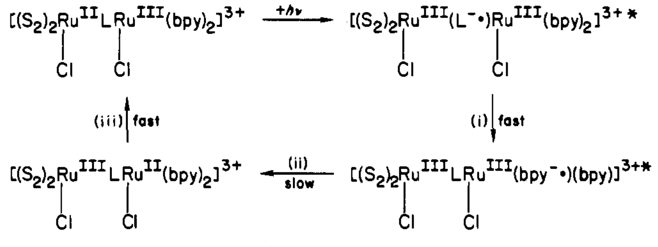
*Sir:*

Ligand-bridged mixed-valence dimers are of interest in the context of electron-transfer studies because the redox sites are held in a well-defined geometry relative to one another, electron transfer between sites is a reversible process, and measurements can be made on the systems as they undergo intramolecular electron transfer. Advantage has been taken of these features to explore the nature of optically induced charge transfer[1-3] and how it is related to the corresponding thermal process on the basis of equations originally derived by Hush.[4-6] However, the direct measurement of intramolecular electron transfer rate constants in such systems has, in the main, proven to be elusive. One approach taken to the problem has involved the application of transient-photolysis techniques to populate a high-energy mixed-valence isomer and to study its subsequent relaxation (eq 1).[7]

EDTA$^{4-}$ = ethylenediaminetetracetate(4−); pyz = pyrazine

(1)

In a related attempt, we observed that for the dimer in eq 2 Ru$^{II}$

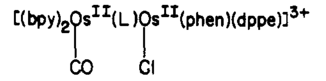


S$_2$ = PhSCH$_2$CH$_2$SPh; bpy = 2,2'-bipyridine; L = 4,4'-bipyridine (4,4'-bpy)

(2)

→ (L) MLCT excitation leads to a bpy-localized MLCT state that subsequently decays to a high-energy, mixed-valence isomer (eq 2(ii)). However, the decay of the MLCT state is relatively slow, and it was not possible to follow the rate of intramolecular relaxation from the mixed-valence isomer to the mixed-valence ground state (eq 2(iii)).

We describe here an alternate approach based on the *creation* of a mixed-valence system in the photolysis step. The systems of interest are ligand-bridged osmium dimers of the type



$$[(bpy)_2\underset{\displaystyle CO}{\underset{|}{Os}}{}^{II}(L)\underset{\displaystyle Cl}{\underset{|}{Os}}{}^{II}(phen)(dppe)]^{3+}$$

phen = 1,10-phenanthroline; dppe = *cis*-Ph$_2$PCH=CHPPh$_2$;

(bpa), 4,4'-bpy

Because of the ligand asymmetry in the dimers, the Os(II) sites have different chromophoric properties: the Os(bpy) and Os(phen) sites have lowest MLCT bands at 425 and 515 nm, respectively. Electronic coupling is clearly weak between the metal sites since the optical spectra of the dimers are nearly the sum of the spectra of the related monomers. Excitation of the dimers at 337 nm using a N$_2$ laser leads to simultaneous excitation of both chromophores. In frozen ethanol–methanol, 4:1 (v/v), excitation of either dimer results in the appearance of the Os$^{III}$(phen$^-$•)-based excited states with emission and decay characteristics that are superimposable with the related monomer. In fluid solution the same situation exists for the bpa-bridged dimer, but for the 4,4'-bpy-bridged dimer, the lowest lying state is an MLCT state based on the flattened, bridging ligand [(bpy)$_2$(CO)Os$^{II}$(4,4'-bpy$^-$•)Os$^{III}$Cl(phen)(dppe)]$^{3+*}$. The details of the glass → fluid induced transition to the flattened state will be discussed in greater detail in a later paper.

Photolysis at 337 nm results in luminescence from both MLCT chromophores. The Os$^{III}$(phen$^-$•) emission is dominant, but weak luminescence from the higher energy MLCT Os$^{III}$(bpy$^-$•) state

**Table I.** Emission Band Maxima and Decay Lifetimes at 77 K in 4:1 CH$_3$CH$_2$OH–CH$_3$OH (v/v)

| compd | $\lambda_{max}$, nm | $\tau$, ns[b] |
|---|---|---|
| [(bpy)$_2$(CO)Os$^{II}$(4,4'-bpy)][PF$_6$]$_2$ | 546 | 5260 |
| [(phen)(Cl)Os$^{II}$(dppe)(4,4'-bpy)][PF$_6$] | 625 | 4070 |
| [(bpy)$_2$(CO)Os$^{II}$(4,4'-bpy)Os$^{II}$(Cl)- | 550 | <10[c] |
| (phen)(dppe)][PF$_6$]$_3$[a] | 625 | 3930 |
| [(bpy)$_2$(CO)Os$^{II}$(bpa)][PF$_6$]$_2$ | 550 | 5430 |
| [(phen)(Cl)Os$^{II}$(dppe)(bpa)][PF$_6$] | 640 | 3800 |
| [(bpy)$_2$(CO)Os$^{II}$(bpa)Os$^{II}$(Cl)- | 550 | 45[d] |
| (phen)(dppe)][PF$_6$]$_3$[a] | 640 | 3740 |

[a] Note that dual emissions are observed for the dimers: an intense component (>90% of total emission) centered at $\lambda$ = 625 nm (L = 4,4'-bpy) or 640 nm (L = bpa) with a weak band on the high-energy side. [b] Obtained from analysis of emission decays except where noted. Error <5% in lifetimes. [c] Lifetime too short to be resolved. [d] Lifetime calculated as $1/k_1$ from Table II. See text for more details.

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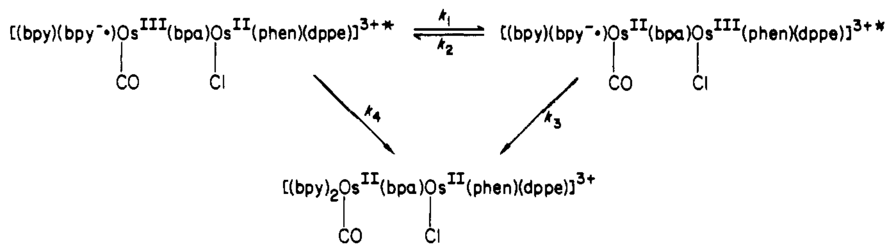
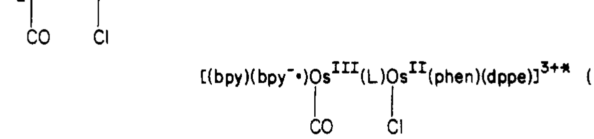
Scheme I



is clearly discernible. However, as shown in Table I, in contrast to the $Os^{III}(phen^{-}\cdot)$ luminescence, the lifetimes of the $Os^{III}(bpy^{-}\cdot)$-based state in the dimers are far shorter than the $Os^{III}(bpy^{-}\cdot)$ lifetimes in related monomers.

The origin of the selectively decreased $Os^{III}(bpy^{-}\cdot)$ lifetime must be in an intramolecular quenching event that follows the initial excitation (eq 3). The quenching process is necessarily intra-

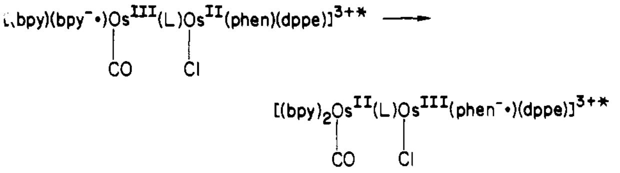


$$[(bpy)_2\underset{\mathrm{CO}}{Os^{II}}(L)\underset{\mathrm{Cl}}{Os^{II}}(phen)(dppe)]^{3+} \xrightarrow{+h\nu} [(bpy)(bpy^{-}\cdot)\underset{\mathrm{CO}}{Os^{III}}(L)\underset{\mathrm{Cl}}{Os^{II}}(phen)(dppe)]^{3+*} \tag{3}$$

molecular, based on the lack of translational mobility in the frozen matrices, the short lifetime for the decay process, and its independence from changes in dimer concentration.

It is interesting to note from eq 3 that the effect of $Os^{II} \rightarrow$ bpy MLCT excitation is to produce a transient mixed-valence dimer, $Os^{III}$–L–$Os^{II}$, which is at the same time an MLCT excited state, $(bpy^{-}\cdot)Os^{III}$. Intrinsically, the MLCT excited state once formed is expected to be relatively long-lived. As previous studies have shown, the ligand environment is such as to give a large energy gap between the excited and ground states, and the nonradiative decay process, which largely determines excited-state decay, $[(bpy)(bpy^{-}\cdot)(CO)Os^{III}\text{–}L\text{–}] \rightarrow [(bpy)_2(CO)Os^{II}\text{–}L\text{–}]$, is relatively slow.[9,10] Note the lifetime data in Table I.

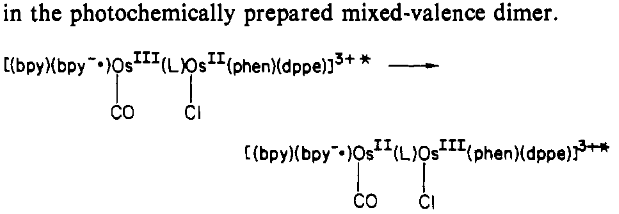
The origin of the decreased $Os^{III}(bpy^{-}\cdot)$ lifetime in the dimers is *not* from energy transfer from the higher energy $Os^{III}(bpy^{-}\cdot)$ state to the lower energy $Os^{III}(phen)$ state



$$[(bpy)(bpy^{-}\cdot)\underset{\mathrm{CO}}{Os^{III}}(L)\underset{\mathrm{Cl}}{Os^{II}}(phen)(dppe)]^{3+*} \longrightarrow [(bpy)_2\underset{\mathrm{CO}}{Os^{II}}(L)\underset{\mathrm{Cl}}{Os^{III}}(phen^{-}\cdot)(dppe)]^{3+*} \tag{4}$$

since excitation spectra show that excitation into the Os(bpy) chromophore does *not* lead to the appearance of emission from the Os(phen)-based MLCT excited state to any significant degree.

The only reasonable alternative appears to be that quenching occurs by a reductive, intramolecular electron-transfer process in the photochemically prepared mixed-valence dimer.



$$[(bpy)(bpy^{-}\cdot)\underset{\mathrm{CO}}{Os^{III}}(L)\underset{\mathrm{Cl}}{Os^{II}}(phen)(dppe)]^{3+*} \longrightarrow [(bpy)(bpy^{-}\cdot)\underset{\mathrm{CO}}{Os^{II}}(L)\underset{\mathrm{Cl}}{Os^{III}}(phen)(dppe)]^{3+*} \tag{5}$$

Energetically, the process in eq 5 appears to be spontaneous. Electrochemical measurements in $CH_3CN$ show that in the dimers the $Os^{II/III}$ oxidations occur at +0.95 V vs. SCE for the Os(phen) site and at +1.67 V for the Os(bpy) site vs. SCE. The potential for the $Os^{III}(bpy)$ excited state as an electron acceptor is estimated to be +1.0 V from the emission energy (2.11 eV) and the potential for the ligand-based $Os^{II}(bpy) \rightarrow Os^{II}(bpy^{-}\cdot)$ couple (−1.12 V). Thus, eq 5 as written is exothermic by approximately 0.05 V.

**Table II.** Temperature Dependence of Scheme I Rate Constants Calculated from Analysis of Emission Decay Data

| | rate constants, $10^7$ $s^{-1}$ | | | |
|---|---|---|---|---|
| *T*, K | $k_1$[a] | $k_2$[b] | $k_3$[b] | $k_4$[c] |
| 77 | 2.2 | 0.35 | 0.95 | 0.019 |
| 95 | 2.3 | 0.38 | 1.2 | 0.021 |
| 100 | 2.2 | 0.32 | 0.91 | 0.021 |
| 110 | 2.3 | 0.46 | 1.2 | 0.023 |
| 120 | 2.3 | 0.52 | 1.2 | 0.030 |
| 130 | 2.9 | 0.64 | 1.5 | 0.037 |
| 140 | 3.3 | 0.52 | 1.2 | 0.037 |
| 150 | 4.2 | 0.62 | 1.2 | 0.042 |
| 160 | 4.8 | 0.98 | 1.1 | 0.044 |

[a] Error limit ±20%. [b] Error limit ±50%. $k_2$ and $k_3$ are more sensitive to errors in measurables than $k_1$. [c] Obtained from emission lifetime measurements on $[(bpy)_2(CO)Os^{II}(bpa)]^{2+}$. Error limits <±10%.

Transient decay of $[(bpy)(bpy^{-}\cdot)(CO)Os^{III}(bpa)Os^{II}(phen)(dppe)Cl]^{3+*}$ follows biexponential kinetics, as has been observed in other bichromophoric systems.[11] The data can be treated on the basis of the kinetic model proposed in Scheme I by using a published nonlinear, multiexponential fitting routine that gives rate constants for the various processes in Scheme I.[11,12] In order to obtain the fits, the values used for $k_4$ were nonradiative decay rates for the monomer $[(bpy)_2(CO)Os^{II}(bpa)]^{2+}$, obtained from emission lifetime measurements. From the fits, $k_1$ and $k_4$, obtained by independent measurement, are reasonably well-defined, but there is a considerable uncertainty in $k_2$ and $k_3$, which is to be expected.

We feel that the multiexponential behavior observed here probably does arise from competing intramolecular events and is not, for example, a matrix effect. Multiexponential behavior in the 4:1 $C_2H_5OH$–$CH_3OH$ glass is *not* observed for the component monomers nor more importantly for the Os(phen) chromophore *in the same dimer in the same medium*. Assuming that our interpretation based on Scheme I is correct, the data in Table II give the rates for the forward and reverse intramolecular electron-transfer steps ($k_1$ and $k_2$, respectively) and for decay of the charge-separated state $[(bpy)(bpy^{-}\cdot)(CO)Os^{II}(bpa)Os^{III}(phen)(dppe)Cl]^{3+}$ ($k_3$). It is at least somewhat reassuring that the rate constant ratio $k_1$:$k_2$, which is equal to the equilibrium constant for the quenching step, is consistent with $\Delta G^{\circ\prime} = -0.05$ eV estimated from room-temperature redox potentials.

It is interesting to note that the intramolecular, mixed-valence electron-transfer rate constant $k_1$, which is reasonably well-defined by the fits, appears to undergo a transition from a temperature-independent to a temperature-dependent region past the glass to fluid transition of the medium (130–140 K). We calculate that,

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(12) Emission decay profiles for $[(bpy)_2(CO)Os(bpa)Os(phen)(dppe)(Cl)]^{3+}$ monitored at 550 nm could best be fit to a triple exponential expression by using an iterative procedure. However, one of the decay components had a relatively long lifetime and accounted for <5% of the total emission decay. This component appears to arise from a small amount of a monomeric impurity or perhaps from residual emission from the $Os^{III}(phen)$ dimer state. Because of the difference in time scales involved, the contribution from the long-lived component was easily separated from that of short-lived, dominant decay components.

for the bpa-bridged dimer, $k_1$ ranges from $2.2 \times 10^7$ to $4.8 \times 10^7$ $s^{-1}$ over the temperature range 77-160 K.

Unfortunately, even at 77 K the intramolecular quenching event for the 4,4′-bpy-bridged dimer is too rapid to be seen with our time resolution (10 ns). In fact, our ability to observe the intramolecular electron-transfer event for the bpa-bridged dimer depends, in part, on the fact that the medium is a frozen matrix. Once the glass to fluid transition is reached, there is a marked decrease in lifetime, resulting in decay processes that are too rapid for our detection capabilities. A contribution to electron trapping arising from the orientation of surrounding solvent dipoles is certainly expected. By inference, a thermally activated component of this contribution may exist that begins to dominate electron transfer once the solvent dipoles become orientationally mobile.

Our observations reinforce those made earlier[7] in suggesting a possible general approach to the problem of measuring intramolecular electron-transfer rate constants in mixed-valence dimers based on excitation of an appropriate chromophore within the dimer. Clearly in the systems chosen for study here, the intramolecular processes are sufficiently rapid that it will be necessary to apply picosecond techniques to the general problem of measuring the transient decays that occur after photolysis.

A final point of note is that the intramolecular process in eq 5 has the effect of creating a remote MLCT state where the excited electron and "hole" within the molecule have been separated by a ligand bridge. This is an important process in that it results in intramolecular charge separation and potentially in long-lived, intramolecular charge storage. However, a puzzling feature is that, once reached, the charge-separated state is relatively short-lived as shown by the $k_3$ values in Table II. We are currently investigating such states in more detail in order to understand the molecular mechanisms that lead to their rapid decay.

**Acknowledgments** are made to the National Science Foundation, Grant No. CHE-8008922, and to the Army Research Office, Durham, NC, Grant No. DAAG29-82-K-0111, for support of this research.

**Registry No.** $[(bpy)_2(CO)Os^{II}(4,4'\text{-bpy})Os^{II}(Cl)(phen)(dppe)][PF_6]_3$, 96532-39-7; $[(bpy)_2(CO)Os^{II}(bpa)Os^{II}(Cl)(phen)(dppe)][PF_6]_3$, 96532-41-1; $[(bpy)_2(CO)Os^{II}(4,4'\text{-bpy})][PF_6]_2$, 96503-61-6; $[(phen)(Cl)Os^{II}(dppe)(4,4'\text{-bpy})][PF_6]$, 96503-63-8; $[(bpy)_2(CO)Os^{II}(bpa)][PF_6]_2$, 96503-65-0; $[(phen)(Cl)Os^{II}(dppe)(bpa)][PF_6]$, 96532-43-3.

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### EPR and Resonance Raman Studies of the (5,10,15,20-Tetraphenylporphinato)ferrate(I) Anion: Formation of a Five-Coordinate Pyridine Adduct

*Sir:*

The nature of highly reduced iron porphyrins is important because of their possible involvement as intermediates in the chemistry of cytochrome P-450 and peroxidases.[2-5] In particular, whether the one-electron-reduction product of Fe(II) porphyrins is best described as an Fe(I) porphyrin or an Fe(II) porphyrin $\pi$ anion radical (or a species intermediate between these two forms) remains unresolved.[6] The EPR spectrum[7] of $[Fe(TPP)]^-$ is characteristic of an axially symmetric spin system with $g_\perp = 2.28$ and $g_\parallel = 1.93$ and, by comparison with low-spin $d^7$ Co(II) porphyrins, has been the basis for a low-spin Fe(I) formulation.[8-10] A recent deuterium NMR study supports the Fe(I) formulation.[11] On the other hand, $[Fe(TPP)]^-$ exhibits an unusual optical spectrum that includes a low-intensity split Soret band and a five-banded visible region,[6,12] which may indicate the presence of substantial electron density on the porphyrin ring. The anion radical formulation is further supported by crystallographic data for $[Na(DB\text{-}18\text{-}crown\text{-}6)(THF)_2]^+[Fe(TPP)]^-$, which shows that the $Fe-N_{pyrrole}$ bond lengths of $[Fe(TPP)]^-$ are shorter than those of Fe(TPP).[13]

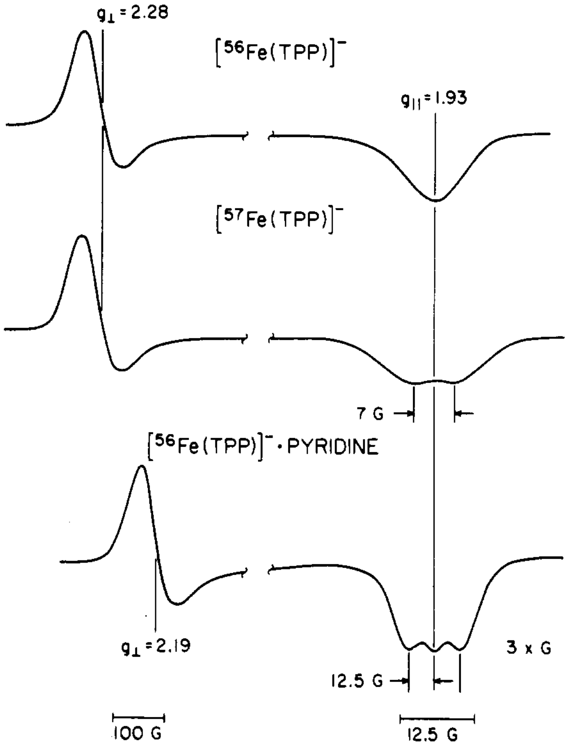

**Figure 1.** Low-temperature (77 K) X-band EPR spectra of DMF glasses of (top) $[^{56}Fe(TPP)]^-$, (middle) $[^{57}Fe(TPP)]^-$, and (bottom) $[^{56}Fe(TPP)]^-$ plus 60 equiv of pyridine. Each sample was 2.0 mM. Conditions: microwave power 18.3 mW; modulation amplitide 2 G.

As a means to resolve the electronic nature of the $[Fe(TPP)]^-$ species, the EPR spectra have been recorded for the $^{57}Fe$-substituted complex and for the $^{56}Fe$ species in the presence of potential axial ligands (pyridine and *N*-MeIm). Resonance Raman spectra of the $[Fe(TPP)]^-$ complex have also been measured.

Figure 1 illustrates the low-temperature (77 K) EPR spectra of $[^{56}Fe(TPP)]^-$, $[^{57}Fe(TPP)]^-$, and $[^{56}Fe(TPP)]^-$ in the presence of pyridine.[14,15] The $g_\parallel$ signal of $[^{57}Fe(TPP)]^-$ is split into a poorly

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(7) Abbreviations: EPR, electron paramagnetic resonance; NMR, nuclear magnetic resonance; Fe(TPP), Fe(II) tetraphenylporphyrin; DB-18-crown-6, dibenzo-18-crown-6; DMF, dimethylformamide; $Me_2SO$, dimethyl sulfoxide; *N*-MeIm, *N*-methylimidazole.

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(14) $^{57}Fe^{III}(TPP)Cl$ was synthesized by a modified procedure of: Burke, J. M.; Kincaid, J. R.; Spiro, T. G. *J. Am. Chem. Soc.* **1978**, *100*, 6077-6083. $^{57}Fe$ was obtained as $^{57}Fe_2O_3$ (90.24% enriched) from Oak Ridge National Laboratories. TPP was purchased from Midcentury (Posen, IL). Fe(TPP) and $[Fe(TPP)]^-$ were generated electrochemically in an inert-atmosphere box as described in ref 12.

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