J. Am. Chem. Soc. **1995,** *117,* 5881−5882

Energy Transfer in Rigidly-Linked Heterodinuclear Ru(II)/Fe(II) Polypyridyl Complexes: Distance and Linkage Dependence

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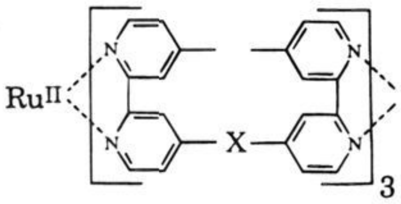
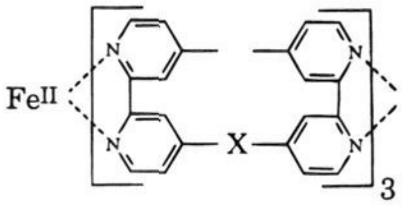
Received December 20, 1994

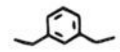
Rates of intramolecular electron and energy transfers in linked donor−acceptor (D−A) systems are dependent on many molecular and environmental parameters.[1] Thus, it is often difficult to design D−A systems where a single parameter can be studied independently of changes in other relevant variables. For example, it is generally exceedingly difficult to alter the connectivity between a donor and acceptor without at the same time altering both the distance separating D and A and their relative orientation. We report here a study of the rates of intramolecular energy transfer from the MLCT excited state of a tris(bipyridine)ruthenium(II) donor to a ground-state tris(bipyridine)iron(II) acceptor within a series of unique, triply-linked dinuclear complexes, **Ia−VIIa**. The existence of the triple linkage renders the complexes rigid, particularly for those having the shortest linking chains (i.e., ones containing two or three atoms).[2] The most significant feature of these complexes, however, is that *the first four members of the series (complexes* **I−IV**) possess virtually identical metal−metal separations and relative ligand orientations. These complexes thus provide a unique opportunity to investigate the role of D−A connectivity in an energy transfer process while maintaining all other relevant parameters virtually constant.



a.



b.

I. X = $(CH_2)_2$
II. X = $(CH_2)_3$
III. X = CH_2-S-CH_2
IV. X = CH_2-O-CH_2
V. X = $(CH_2)_4$
VI. X = $(CH_2)_5$
VII. X = 

The X-ray structure of **Ib** has been reported previously.[2] Attempts to structurally characterize complexes **IIb−IVb** have met with limited success. Complexes **IIIb** and **IVb** have not yet yielded diffraction quality crystals; however, a low-quality structure of **IIb** has been obtained. In this structure, the triflate anions and the methylenes in the linkage are significantly disordered, but the two metals and their associated bipyridine ligands refine well.

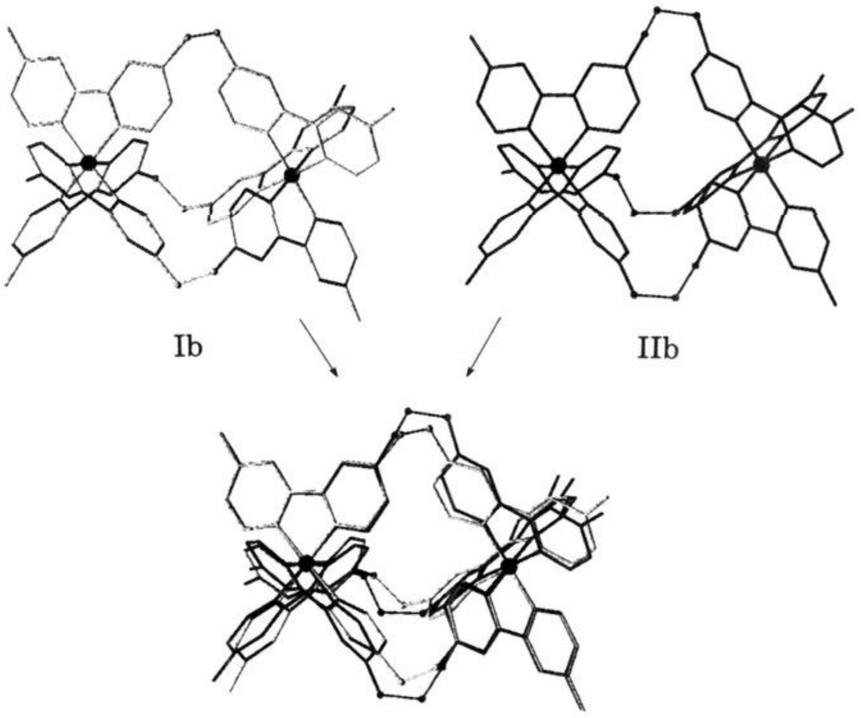


Figure 1. Structures of **Ib** and **IIb,** and their superposition, obtained from molecular modeling. Hydrogens have been omitted for clarity.

Molecular mechanics calculations employing software from Biograf[3] were conducted on all of the dinuclear Fe−Fe and Ru−Fe complexes. For complex **Ib**, the calculated structure is virtually superimposable with the structure determined by X-ray diffraction. Likewise, the modeled structure of **IIb** reproduces equally well the portions of the X-ray structure that are not disordered. The fact that the molecular mechanics calculations faithfully reproduce the X-ray structures of **Ib** and **IIb** gives us considerable confidence that these calculations produce meaningful representations of the solution structures of the remaining complexes.

Figure 1 shows the modeled structures of **Ib** and **IIb** along with their superposition. This figure nicely illustrates that both the metal−metal distances and the relative orientations of the bipyridine ligands are nearly identical *despite the fact that the bridges are quite different* (i.e., two vs three methylenes). In fact, the calculations show that complexes **Ia−IVa** and **Ib−IVb** are all virtually isostructural *except for the bridging linkages*. Thus, complexes **Ia−IVa** constitute a D−A series in which all of the parameters that are expected to influence energy transfer rates remain constant *except* for their connectivity.

The time-correlated single photon counting system used to measure the RuL_3 MLCT emission lifetimes has been described elsewhere.[4] Solutions employed in emission lifetime studies were prepared by dissolving solid samples of the PF_6^- salt of each Ru(II)−Fe(II) complex (**Ia−VIIa**) in O_2-free dichloroethane and sealing the samples under vacuum. Emission decay curves were obtained at room temperature following excitation at 315 nm near the π,π^* absorption maximum with detection at 630 nm near the RuL_3 MLCT emission maximum. Each emission decay could be fit to a single exponential (>85%) plus a small constant component. The relative amount of this time-independent component varied between sample preparations and thus is ascribed to the presence of a small amount of long-lived luminescent impurity.

Table 1 lists the emission decay rates, k_q, for complexes **Ia−VIIa.** For the iron-free analogs of **Ia−VIIa**, the lifetime of the RuL_3 MLCT state is >1 μs. Thus, within experimental error, the measured emission decay rates equal the rates of MLCT state quenching. Figure 2 is a plot of log k_q vs the Ru−Fe distance obtained from the molecular modeling calculations. There are two aspects of these data that are particularly noteworthy. First is the functional dependence of k_q on distance, and second is the lack of dependence of k_q on the nature of the bridging linkage.

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Table 1

complex	calcd Ru−Fe distance (Å)	k_q (ns^{-1})
Ia	7.61	2.44
IIa	7.57	2.87
IIIa	7.59	2.71
IVa	7.50	2.94
Va	8.70	0.370
VIa	9.23	0.075
VIIa	9.89	0.029

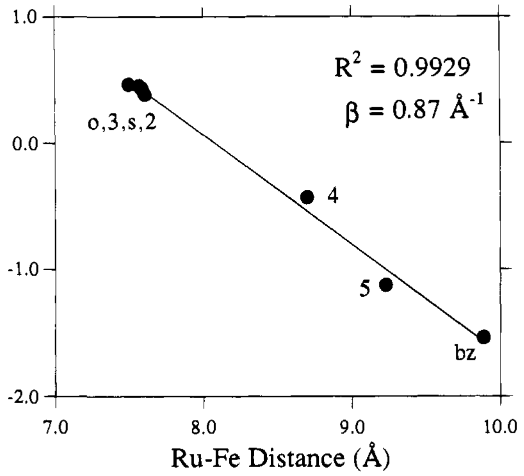

Figure 2. Plot of the logarithm of the emission decay rate (ns^{-1}) vs the Ru−Fe separation as obtained from molecular modeling calculations. Quenching rates were measured in O_2-free dichloroethane solvent (2, **Ia**; 3, **IIa**; s, **IIIa**; o, **IVa**; 4, **Va**; 5, **VIa**; bz, **VIIa**).

Electron transfer quenching of the RuL_3 MLCT excited state by the FeL_3 can be ruled out since, in the most favorable case, this process would be endothermic by >100 mV.[5] Electronic energy transfer quenching generally occurs by one of two mechanisms: coupling of the transition multipoles between the donor and the acceptor[6] or electron exchange between the donor and acceptor.[7] The strongest multipole component of the former process is the dipole−dipole coupling transfer (Förster).[6] Both processes depend, in similar ways, on the spectral overlap of the acceptor absorption and the donor emission.[8] The ground-state visible absorption spectra of **Ia**−**VIIa** are all, within experimental error, identical; consequently, it is assumed that the spectral overlap term is constant within the series.

In their simplest forms, each of these two energy transfer mechanisms has a distinctly different dependence on D−A separation, r.[8] Exchange transfer quenching rates should fall off approximately as $e^{-\beta r}$, whereas dipolar quenching should decrease as $1/r^6$. The data in Figure 2 show that for **Ia**−**VIIa**, the quenching rate falls off exponentially as the metal−metal separation increases. Furthermore, log k_q vs log r plots indicate that a value of $n = 17$ is required to obtain a reasonable fit of k_q to $1/r^n$ when r is taken as the metal−metal separation (which is roughly the same as the estimated distance separating the transition dipoles). If the donor and acceptor are approximated as spheres and one considers the closest edge−edge separation (which grossly underestimates the appropriate distance), a value of $n = 9$ is obtained from such a fit. This value is still too large to be rationalized by a Förster model, even if higher multipole interactions (e.g., quadrupole−quadrupole, etc.) were to be considered. Furthermore, since the present process is nominally a triplet−triplet transfer, a dipolar mechanism would be spin forbidden.[8,9]

Proceeding, then, with the assumption that the MLCT state of the RuL_3 is being quenched by an exchange energy transfer mechanism, it is noteworthy, indeed, that k_q *is independent of the nature of the bridges and appears to depend only on the D−A separation.* These results are particularly striking for complexes **Ia**−**IVa**, where k_q and the Ru−Fe separation remain nearly invariant while both the numbers of bonds in the bridges and the atoms which make up the bridges vary within the series.

The number of energy and electron transfer studies conducted on rigid, intramolecular D−A systems is now considerable.[10] In a significant number of these studies, electron superexchange through the σ-bonding framework of the bridge has been implicated in the transfer mechanism.[10a,c,f−h] To our knowledge, the present study is the first where strong experimental evidence exists suggesting that an exchange process is occurring *without* significant participation of the σ-bonding linkage. The β value obtained from the log k_q vs r fit, 0.87 Å^{-1}, is much too small to be consistent with a purely "through-space" electron exchange process. The most reasonable conclusion, therefore, is that a superexchange pathway exists, but it does not involve the intramolecular linkages. Most likely it involves a pathway through the solvent.

Finally, we have recently conducted preliminary spectral studies on mixed-valent (3+/2+) analogs of the dinuclear iron complexes **Ib**−**IVb**.[11] These species exhibit very weak intervalence charge transfer transitions in the near-IR. Initial consideration of these spectra suggests that this optically-induced electron transfer (between the 3+ and 2+ metal centers) is also independent of the bridging linkage.

Acknowledgment. The authors would like to thank Professor Walter S. Struve and Dr. Marshall Newton for helpful discussions and Professor David F. Kelley for access to the SPC apparatus. Support of this work by the USDOE, Office of Basic Energy Sciences (DE-FG02-92ER14301) is gratefully acknowledged.

JA944094M

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