weak interactions with ca. 30 water molecules in the first hydration shell. Importantly, the success of the OPLS potential functions in this and prior contexts is auspicious for their use in describing peptide-water interactions for simulations of myriad biochemical systems. The present work also completes the parameterization of potential functions needed to describe interfacial systems including micelles that contain amphiphiles with ammonium or

carboxylate head groups.

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CHEMICAL KINETICS

Excited-State Electron Transfer in Ligand-Bridged Dimeric Complexes of Osmium

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The photophysical properties of the unsymmetrical ligand-bridged Os dimers, $[(bpy)_2(CO)Os^{II}(L)Os^{II}(phen)(dppe)(CI)]^{3+}$ and $[(bpy)_2(CO)Os^{II}(L)Os^{III}(phen)(dppe)(CI)]^{4+}$ (L = 4,4'-bipyridine (4,4'-bpy) or 1,2-bis(4-pyridyl)ethane (bpa), bpy = 2,2'-bipyridine, phen = 1,10-phenthroline, and dppe = 1,2-bis(diphenylphosphino)-*cis*-ethene), have been investigated by using a variety of techniques. In the (II,II) dimers, two independent metal to ligand charge transfer (MLCT) chromophores are present, based upon localized $d\pi(Os) \rightarrow phen$ and $d\pi(Os) \rightarrow 2,2'$ -bpy transitions at the respective metal centers. The results of transient absorption and emission experiments suggest that quenching of the higher energy, Os(bpy) localized MLCT state does not occur by Os(bpy) MLCT \rightarrow Os(phen) MLCT energy transfer which is energetically favorable. Rather, the quenching have been measured for the bpa-bridged dimer at low temperatures in a glassy solvent. The excited-state behavior of the (II,II) dimers (L = 4,4'-bpy or bpa) is similar in frozen solutions. However, from steady-state transient emission and transient absorption data, past the glass to liquid transition the 4,4'-bpy bridging ligand in the 4,4'-bpy dimer "flattens" and acts as an electron acceptor. The flattening and concomitant intramolecular quenching processes in fluid media are rapid compared to the lifetime of the initially populated CT excited state. In the mixed-valence (II,III) dimers the spectroscopically observed Os(bpy) MLCT excited state is relatively unperturbed by the adjacent Os^{III}(phen) site and there is no evidence for quenching by any of a number of energetically favorable pathways.

Introduction

The results of studies on bichromophoric and chromophorequencher molecules have addressed a series of fundamental questions concerning the effect of distance, orientation, and energy change on rates of intramolecular energy¹ and electron transfer.² While many well-documented examples exist for organic systems, relatively few studies have been conducted based on transitionmetal complexes.³ To date, most investigations using bichromophoric transition-metal complexes have focused on d-d energy transfer⁴ or on optically induced charge transfer between metal sites in mixed-valence dimers.⁵

Polypyridyl complexes of $d\pi^6$ transition metals—Ru(II), Os(II), Re(I), ...—have low-lying metal to ligand charge transfer (MLCT) excited states which have properties which make them attractive candidates for studies involving intramolecular electron or energy transfer. The excited states are long lived, luminescent, and relatively photochemically inert and are known to undergo excited-state electron transfer⁶ although their involvement in energy-transfer processes has received less attention.^{6b,7}

 ⁽a) Stryer, L.; Haughland, R. P. Proc. Natl. Acad. Sci. U.S.A. 1967, 58, 719.
 (b) Latt, S. A.; Cheung, H. T.; Blout, E. R. J. Am. Chem. Soc. 1965, 87, 995.
 (c) Schwartz, F. P.; Gouterman, M.; Muljani, Z.; Dolphin, D. Bioinorg. Chem. 1972, 2, 1.
 (d) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. J. Org. Chem. 1980, 45, 3933.
 (2) (a) Joran, A.; Leland, B.; Geller, G.; Hopfield, J. J.; Dervan, P. B. J.

^{(2) (}a) Joran, A.; Leland, B.; Geller, G.; Hopfield, J. J.; Dervan, P. B. J. Am. Chem. Soc. 1984, 106, 6090. (b) Wasielewski, M. R.; Niemczyk, M. P.; J. Am. Chem. Soc. 1984, 106, 5043. (c) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B., in press. (d) McIntosh, A. R.; Siemiarczuk, A.; Bolton, J. R.; Stillman, M. J.; Ho, T-F.; Weedon, A. C. J. Am. Chem. Soc. 1983, 105, 7215. (e) Seimiarczuk, A.; McIntosh, A. R.; Ho, T.-F.; Stillman, M. J.; Roach, K. J.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S. J. Am. Chem. Soc. 1983, 105, 7224. (f) Moore, T. A.; Gust, D.; Mathis, P.; Mialocq, J.-C.; Chachaty, C.; Bensasson, R. V.; Land, E. J.; Doizi, D.; Liddell, P. A.; Lehman, W. R.; Nemeth, G. A.; Moore, A. L. Nature 1984, 307, 630. (g) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. J. Am. Chem. Soc. 1984, 106, 3047. (h) Vanderauwera, P.; DeSchryver, F. C.; Weller, A.; Winnick, M. A.; Zacharcusse, K. A. J. Phys. Chem. 1984, 88, 2964. (i) Hush, N. S. Coord. Chem. Rev. 1985, 64, 135. (j) Hush, N. S.; Paddon-Row, M. N.; Cotsaris, E.; Overing, H.; Verhoeven, J. W.; Heppener, M. Chem. Phys. Lett. 1985, 117, 8. (k) Franco, C.; McLendon, G. Inorg. Chem. 1984, 23, 2370.

^{(3) (}a) Curtis, J. C.; Bernstein, J. S.; Schmehl, R. H.; Meyer, T. J. Chem. Phys. Lett. 1981, 81, 48. (b) Curtis, J. C.; Bernstein, J. S.; Meyer, T. J. Inorg. Chem. 1985, 24, 385. (c) Curtis, J. C. Ph.D. Dissertation, University of North Carolina at Chapel Hill, 1980.

⁽⁴⁾ Moore, K. J.; Lee, L.; Figard, J. E.; Gelroth, J. A.; Stinson, A. J.; Wholens, H. D.; Petersen, J. D. J. Am. Chem. Soc. 1983, 105, 2274.

^{(5) (}a) Meyer, T. J. Acc. Chem. Res. 1978, 11, 94. (b) Taube, H. In "Tunneling in Biological Systems"; Chance, B. et al., Eds.; Academic: New York, 1979; p 173. (c) Creutz, C. Prog. Inorg. Chem. 1983, 30, 1.

<sup>York, 19/9; p. 1/3. (c) Creutz, C. Prog. Inorg. Cnem. 1950, 50, 1.
(6) (a) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. J. Am. Chem. Soc. 1979, 101, 4815. (b) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. Coord. Chem. Rev. 1975, 15, 321. (c) Meyer, T. J. Prog. Inorg. Chem. 1983, 30, 389.
(d) Sutin, N.; Creutz, C. Pure Appl. Chem. 1980, 52, 2717. (e) Sutin, N. J. Photochem. 1979, 10, 19. (f) Kalyanasundaran, K. Coord. Chem. Rev. 1982, 46, 159.</sup>

 ^{(7) (}a) Bolletta, F.; Maestri, M.; Moggi, L.; Balzani, V. J. Am. Chem. Soc.
 1973, 95, 7864. (b) Demas, J. N.; Adamson, A. W. J. Am. Chem. Soc. 1971, 93, 1800.

We have prepared two unsymmetrical ligand-bridged Os^{II} dimers based on the unit

where bpy is 2,2'-bipyridine, phen is 1,10-phenanthroline, and



Because of the difference in coordination environments at the two Os sites, there is a moderate difference in energy between the "localized" MLCT excited states, e.g., [(bpy -)(CO)Os^{III}(L)- $Os^{II}(phen)(dppe)(Cl)]^{3+*}$ (E ~ 2.1 eV) and [(bpy)₂(CO)Os^{II}-(L)Os^{III}(phen⁻¹)(dppe)(Cl)]^{3+*} ($E \sim 1.9$ eV). Excited- and ground-state redox potentials are also different at the two sites. Following selective excitation at the high-energy chromophore in the dimers, several possible processes can occur including intramolecular energy transfer

$$[(bpy)(bpy^{-})(CO)Os^{III}(L)Os^{II}(phen)(dppe)(CI)]^{3+*} \rightarrow [(bpy)_2(CO)Os^{II}(L)Os^{III}(phen^{-})(dppe)(CI)]^{3+*} (1)$$

or electron transfer

$$[(bpy)(bpy^{-})(CO)Os^{III}(L)Os^{II}(phen)(dppe)(Cl)]^{3+*} \rightarrow [(bpy)(bpy^{-})Os^{II}(L)Os^{III}(phen)(dppe)(Cl)]^{3+} (2)$$

Experimental Section

A. Materials. Solvents for preparative experiments were reagent grade; solvents used in electrochemical and spectroscopic measurements were Burdick and Jackson spectroquality. The EtOH/MeOH 4:1 (v:v) mixture used for low-temperature spectroscopy was prepared from spectroquality solvents which were carefully dried by distillation from Mg/I_2 and subsequent drying over activated powdered (EtOH) or bead (MeOH) molecular sieves. Supporting electrolytes ($[NEt_4](ClO_4)(TEAP)$ and KPF_6) were recrystallized prior to use. All complexes were purified as described below after preparation.

B. Preparations. The Os complexes described were synthesized by using modifications of synthetic procedures described elsewhere.^{9,10} For the series of complexes of the type $[(bpy)_2Os^{II} (CO)L]^{2+or+}$ the stereochemistry at Os is cis as verified in several cases by ¹H NMR.

 $[(bpy)_2Os(CO)L][PF_6]_2$, L = 4,4'-bpy and bpa. The carbonyl monomers were prepared via reaction of excess L with $[(bpy)_2Os(CO)(CF_3SO_3)][CF_3SO_3]$. The preparation of the triflate precursor complex has been previously described.¹⁰ Triflate salt, 500 mg (0.6 mmol), and 12 mmol of L (20-fold excess) were heated at reflux under N_2 in dimethylformamide (DMF) for 8-12 h. The reaction mixture was cooled and the DMF removed by rotary evaporation. The product was dissolved in 50 mL of H_2O and excess ligand removed by filtration leaving a clear yellow solution. The product, [(bpy)₂Os(CO)L][PF₆]₂, was precipitated by the addition of excess NH_4PF_6 and collected on a sintered glass funnel. The salt was purified by elution from an alumina column using CH₃CN solvent. Yield after purification was 60-70%. Anal. Calcd for [(bpy)₂Os(CO)(4,4'-bpy)[PF₆]₂: C, 38.11%; H, 2.46%;

N. 8.61%. Found: C. 37.72%; H. 2.27%; N. 8.35%. Calcd for $[(bpy)_2Os(CO)(bpy)][PF_6]_2$: C, 39.43%; H, 2.79%; N, 8.36%. Found: C, 38.07%; H, 3.02%; N, 8.05%.

 $[(phen)Os(dppe)(Cl)L][PF_6], L = 4,4'-bpy and bpa.$ Starting Materials. (a) Os(phen)Cl₄. One gram (2.3 mmol) of [N-H₄]₂[OsCl₆] was dissolved in 50 mL of 3 N HCl at 70 °C. To this a solution of 0.42 g (2.3 mmol) 1,10-phenanthroline in 10 mL of 3 N HCl was added slowly. During the addition, the mixed salt [(phenH)(NH₄)][OsCl₆] precipitated from solution. The solution was cooled to 0 °C and the salt collected by filtration. The salt was washed with cold 3 N HCl, H₂O, and ether and subsequently dried at 70 °C under vacuum for 24 h. (phen)OsCl₄ was obtained by the solid-state pyrolysis of the well-dried salt at 290 °C in a NaNO₂ molten salt bath under N₂. During pyrolysis the color changes from dark red to brown; the reaction was judged to be complete when red material had disappeared (5-8 h). Yield after pyrolysis, 1.10 g (90%).

(b) cis-(phen)Os(dppe)Cl₂. Os(phen)Cl₄, 410 mg, and 450 mg of 1,2-bis(diphenylphosphino)-cis-ethene (1.6 mmol) were heated at reflux in 40 mL of bis(2-methoxyethyl) ether under N_2 for 3 h. The solution was cooled and the precipitate collected on a sintered glass funnel. The precipitate was slowly washed through the filter with 50 mL of CH_2Cl_2 and precipiated by addition to 250 mL of ether. The precipitate was collected on a sintered glass funnel and dried in vacuo, yield 275 mg (41%).

(c) $[(phen)Os(dppe)(Cl)(L)][PF_6], L = 4,4'-bpy, bpa.$ cis-(phen)Os(dppe)Cl₂, 80 mg, (0.1 mmol) and 2 mmol of L (20-fold excess) were heated at reflux in 10 mL of 2-methoxyethanol under N_2 for 6 h. The reaction mixture was cooled and added to 40 mL of H_2O . The product was removed by precipitation via addition of excess NH₄PF₆ (aqueous) collected on a sintered glass funnel and dried in vacuo. Cyclic voltammetry showed that the product was a mixture of cis and trans isomers where cis and trans refer to the relative orientation of the added ligand L and the phosphine ligand. The trans isomer was isolated by careful column chromatography on alumina using 1:1 acetonitrile/toluene as eluant followed by a preparative scale alumina TLC separation using 30% acetonitrile/toluene mobile phase.



As illustrated in the structures above, for convenience the trans isomer is defined to have stereochemistry in which the ligand L is trans to one of the P atoms of the phosphine ligand. In the cis isomer the ligand L is cis to both P atoms. Yield after purification, ~25%. Anal. Calcd for [(phen)Os(dppe)(Cl)(4,4'-bpy)]-[PF₆]·3H₂O: C, 49.79%; H, 3.80%; N, 4.84%. Found: C, 49.47%; H, 3.55%; N, 4.72%. Calcd for [(phen)Os(dppe)(Cl)(bpy)]-[PF₆]·2H₂O: C, 51.42%; H, 3.94%; N, 4.80%. Found: C, 51.91%; H, 3.91%; N, 4.72%.

 $[(bpy)_2(CO)Os(L)Os(phen)(dppe)(Cl)][PF_6]_3, L = 4,4'-bpy,$ bpa. The dimers were prepared by the reaction between $[(bpy)_2Os(CO)L][PF_6]_2$ and $(phen)Os(dppe)Cl_2$. In a typical preparation 0.2 mmol of [(bpy)Os(CO)L][PF₆]₂ and 0.2 mmol of (phen)Os(dppe)Cl₂ were heated at reflux in 20 mL of 2methoxyethanol under N_2 for 10 h. The solution was cooled and poured into 50 mL of aqueous NH_4PF_6 . The product was collected, and dried in vacuo. As noted below, cyclic voltammetry of the reaction product suggested that both cis and trans isomers were present.

Purification of the dimers proved to be quite difficult due to the presence of (1) strongly luminescent monomeric impurities $(e.g., [(bpy)_2Os(CO)L]^{2+}, L = 4,4'-bpy, bpa, NCCH_3, etc.)$ and (2) formation of both cis and trans isomers for the [(L)Os-(phen)(dppe)Cl]⁺ site. Purification was finally achieved by utilizing reversed phase HPLC in a semipreparative manner based on a method described recently for the separation of various

⁽⁸⁾ This work has appeared in part in a preliminary communication:

<sup>Schanze, K. S.; Neyhart, G. A.; Meyer, T. J. Inorg. Chem. 1985, 24, 2121.
(9) (a) Caspar, J. V. Ph.D. Dissertation, University of North Carolina at</sup> Chapel Hill, 1982. (b) Kober, E. M., Ph. D. Dissertation, University of North Carolina at Chapel Hill, 1981. (c) Caspar, J. V.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J., submitted for publication. (10) Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. Organo-

metallics 1983, 1, 551.

substituted 2,2'-bipyridine complexes of Ru using a C_{18} bonded stationary phase under ion-pairing conditions.^{11,17} The HPLC separation utilized a Whatman C-18 ODS column with 27.5% $THF/H_2O/0.015$ M methanesulfonic acid as the mobile phase. In a typical chromatographic run, 10 mg of the reaction product (as the Cl⁻ salt) in 500 μ l of H₂O was injected; after collection of the purified dimer from 5 to 6 chromatographic runs the product was precipitated from the THF/H2O/MSA solvent via addition of NH_4PF_6 (aqueuous). From the properties of related monomers it appears most likely that in the dimers isolated following HPLC separation the stereochemistry at the Os^{II}-phen site is trans and the structure is as shown below where the N chelate at the Os-CO site is 2,2'-bpy and at the other site 1,10-phen.



Anal. Calcd for [(bpy)₂(CO)Os(4,4'-bpy)Os(phen)(dppe)-(Cl)][PF₆]₃: C, 43.05%; H, 2.81%; N, 5.82%. Found: C, 41.91%; H, 3.18%; N, 6.01%. Calcd for [(bpy)₂(CO)Os(bpy)Os-(phen)(dppe)Cl)][PF₆]₃·3H₂O: C, 42.49%; H, 3.19%; N, 5.59%. Found: C, 42.24%; H, 3.24%; N, 5.52%

Mixed Valence Ions, $[(bpy)_2(CO)Os^{II}(L)Os^{III}(phen)(dppe) Cl^{4+}$, L = bpa, 4,4'-bpy. Mixed valence ions were generated in solution by electrolysis immediately prior to spectroscopic work. In a typical preparation, 3.0 mg of a dimer was dissolved in 3.0 mL of CH₃CN/0.1 M KPF₆ ([dimer] $\sim 5 \times 10^{-4}$ M). The solution was subjected to oxidative electrolysis at +1.2 V vs. SSCE (Pt gauze electrode, using a "W" type cell) until the current leveled off at $\leq 5\%$ of the initial value; calculated *n* values were generally within 10% of 1.0.

C. Electrochemistry. Cyclic voltammetry (CV) and differential pulse voltammetry (DP) were conducted with a PAR Model 174A polarographic analyzer. Electrolysis and coulometric measurements were made with a PAR Model 179 digital coulometer. CV and DP were conducted with a Pt disk working, Pt wire auxiliary, and saturated sodium calomel reference (SSCE) electrodes in a one-compartment cell. Electrolysis and coulometry were conducted in a three-compartment cell with a Pt gauze working electrode. Solutions were in CH₃CN or DMF solvents with 0.1 M TEAP or KPF₆ as supporting electrolyte.

D. Optical Spectra. UV-visible spectra were recorded on a HP 8450A diode array spectrometer. Near-IR spectra were obtained with a CARY 17 recording spectrometer. Corrected emission spectra were obtained with an SLM Instrument Model 8000 photon-counting fluorimeter. Low-temperature emission spectra of samples in a 4:1 EtOH/MeOH glass were obtained with cells contained in an Oxford Instruments optical cryostat. Spectral fits of the low-temperature emission spectra were made by using a procedure previously described.¹² Corrected excitation spectra were obtained by using the SLM fluorimeter in a ratio recording mode with Rhodamine B dissolved in glycerol (C = 5 \times 10⁻³ M, solution contained in triangular cell) as a quantum counter.

E. Transient Emission and Absorption Spectroscopy. Emission lifetimes were obtained following excitation with a pulsed N₂ laser (337 nm). Detection and data analysis were conducted by literature procedures.9,13

Transient absorption measurements were obtained by using either the second or third harmonics of a Q-switched Nd:YAG laser for excitation (532 or 355 nm, respectively). The optical monitoring system and data analysis procedures have been described.14,15

TABLE I. E_{1/2} Values in V vs. SSCE at Room Temperature

	oxida- tive ^{a,b}		reductive ^{a,c}			
	E_1	E_2	$\overline{E_1}$	E_2	E_3	E_4
[(bpy) ₂ Os(CO)(4,4'- bpy)] ²⁺	1.72		-1.04	-1.21	-1.51	
[(phen)Os(dppe)Cl(4,4'- bpy)] ⁺	0.97		-1.46 ^d	-1.82 ^d		
[(bpy) ₂ (CO)Os(4,4'- bpy)Os(phen)(dpp)- (Cl)] ³⁺	1.03	1.75	-1.02	-1.16	-1.29	-1.45 ^d
$[(bpy)_2Os(CO)(bpa)]^{2+}$	1.67		-1.00	-1.18	-1.82	
[(phen)Os(dppe)Cl- (bpa)] ⁺	0.95		-1.38 ^d			
[(bpy) ₂ (CO)Os(bpa)Os- (phen)(dppe)(Cl)] ³⁺	0.93	1.64	-1.02	-1.19	-1.37 ^d	

^a All potentials vs. SSCE, saturated sodium calomel electrode. $E_{1/2}$ values were calculated as the midpoint between peak potentials for the oxidative and reductive waves in cyclic voltammetry. E_1 and E_2 for the oxidative processes refer to Os(III)/(II) couples of which there are two in the dimers. The reductive couples are a series of polypyridine-based b CH₃CN/0.1 M TEAP. c DMF/0.1 M TEAP. reductions. ^d Chemically irreversible apparently because of Cl⁻ loss.



Figure 1. Absorption spectra of 4,4'-bpy complexes, CH_2Cl_2 solvent. (---) [(phen)Os(dppe)(Cl)(4,4'-bpy)]⁺; (---) [(bpy)_2Os(CO)(4,4'bpy]²⁺; (-) [(bpy)₂(CO)Os(4,4'-bpy)Os(phen)(dppe)(Cl)]³⁺.



Figure 2. Absorption spectra of bpa complexes, CH_2Cl_2 solvent. (----) $[(phen)Os(dppe)(Cl)(bpa)]^+; (---) [(bpy)_2Os(CO)(bpa)]^{2+}; (--)$ [(bpy)₂(CO)Os(bpa)Os(phen)(dppe)(Cl)]³

Results and Discussion—Background

A. Electrochemistry. $E_{1/2}$ values obtained by cyclic or differential pulse voltammetry are tabulated in Table I. $E_{1/2}$ values for the Os(III/II) couples in the dimers (E_1 (oxidative)) are close

⁽¹¹⁾ Valenty, S. J.; Behnken, P. E. Anal. Chem. 1978, 50, 834.
(12) Caspar, J. V.; Westmoreland, T. D.; Allen, G. H.; Bradley, P. G.; Meyer, T. J.; Woodruff, W. H. J. Am. Chem. Soc. 1984, 106, 3492 (13) Demas, J. N. "Excited State Lifetime Measurements"; Academic:

New York, 1983; Chapter 5.

⁽¹⁴⁾ Fenster, A.; LeBlanc, J. C.; Taylor, W. B.; Johns, H. E. Rev. Sci. Instrum. 1973, 44, 689.

^{(15) (}a) Schanze, K. S. Ph.D. Dissertation, University of North Carolina at Chapel Hill, 1983. (b) The sample and hold voltmeter was designed and built in-house. It is similar to a device described recently; see: Luthjens, L. H.; Hom, M. C.; Vermeulen, M. Rev. Sci. Instrum. 1984, 55, 495.

⁽¹⁶⁾ Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer,

T. J. J. Am. Chem. Soc. 1980, 102, 7383.
 (17) Ghosh, P. K.; Brunschwig, B. S.; Chou, M.; Creutz, C.; Sutin, N. J. Am. Chem. Soc. 1984, 106, 4772.

TABLE II. UV-Visible Absorption Data and Assignments^a

complex	λ_{max} , nm	ϵ , M ⁻¹ cm ⁻¹	assignment ^c
$[(bpy)_2Os^{II}(CO)(4,4'-bpy)]^{2+}$	420	4.0×10^{3}	$Os \rightarrow bpy MLCT$
	350	9.0×10^{3}	$Os \rightarrow 4,4'$ -bpy MLCT
	315 (sh)	2.0×10^{4}	$IL\pi,\pi^*$
	298	2.5×10^{4}	$IL\pi,\pi^*$
	245-260	2.9×10^{4}	$IL\pi,\pi^*$
$[(phen)Os^{11}(dppe)Cl(4,4'-bpy)]^+$	515 (sh)	3.0×10^{3}	$Os \rightarrow phen MLCT$
	410	9.2×10^{3}	$Os \rightarrow phen MLCT$
	350 (sh)	6.5×10^{3}	$O_s \rightarrow 4.4'$ -bpy MLCT
	295 (sh)	9.5×10^{3}	IL. π . π^*
	265	2.7×10^{4}	$IL\pi.\pi^*$
$[(bpy)_2(CO)Os^{II}(4,4'-bpy)Os^{II}(phen)(dpp)Cl]^{3+}$	510	9.0×10^{3}	$Os(phen) \rightarrow 4.4'$ -bpy MLC
	380-400	1.4×10^{4}	$Os(phen) \rightarrow phen MLCT$ $Os(phy) \rightarrow phy MLCT$
	315 (sh)	21×10^{4}	$U = \pi^*$
	295	3.1×10^4	$I = \pi, \pi$
	260	4.7×10^{4}	$I = \pi^*$
$[(hny)_{a}(CO)Os^{II}(4.4/hny)Os^{III}(nhen)(dnne)C1]^{4+b}$	≈1700	$< 2 \times 10^{2}$	$d\pi - d\pi$
	750-800	6×10^2	IT
	580	1.2×10^{3}	IMCT
	445 (sh)	45×10^{3}	$O_{\rm s}({\rm hny}) \rightarrow {\rm hny} {\rm MLCT}$
	375	1.4×10^4	$O_{s}(h_{y}) \rightarrow 4.4'_{h_{y}} MICT$
	315 (sh)	1.4×10 2.7 × 10 ⁴	$U = \sigma^*$
	208	2.7×10 2.2×104	Π_{π},π^{-}
	250	3.3×10	$\Pi_{\pi,\pi}$
$[(nben) Os^{III}(dnne) Cl(4.4', bny)]^{2+b}$	~1700	4.4×10^{-10}	d = d =
	~1700	12×10^{-1}	
$[(hny) \cap e^{II}(\cap \cap)(hng)]^{2+}$	125	1.2×10^{-1}	$D_{\rm MCI}$
	$\frac{425}{340}$ (sh)	3.3×10^{-1}	$O_{S} \rightarrow bpy$ MLCT
	340(sh)	1.3×10	U = -*
	208	$2.7 \times 10^{-2.7}$	$\Pi_{\pi,\pi}$
	270	3.0×10^{-1}	$1L\pi,\pi^{-1}$
	203 255 (ch)	3.3×10^{-1}	$1 \perp \pi, \pi$
$[(nhen)Os^{II}(dnne)O(hne)]^{+}$	255 (SII) 515	2.0×10^{-1}	$1L\pi,\pi^{-1}$
[(piter)Os (uppe)Ci(upa)]	100	2.1×10^{-5}	$O_{s} \rightarrow phen MLCT$
	400	5.7×10^{-5}	$O_{s} \rightarrow pnen MLCT$
	370 205 (ch)	3.0×10^{-1}	U = -*
	275 (81)	1.5×10^{4}	$1 \perp \pi, \pi$
$[(hny) (CO)Oc^{II}(hnc)Oc^{II}(nhen)(dnne)CII^{3+}$	520	2.5×10	$\Omega_{\pi}(\pi h \circ \pi) \rightarrow \pi h \circ \pi M I C T$
	320	1.3×10^{-1}	$O_{s}(phen) \rightarrow phen MLCT$
	405	8.0 × 10	$Os(bpy) \rightarrow bpy MLCT$
	340	1.3×10^{4}	Os(bpy) → bpa MLCT
	310 (sh)	2.9×10^{4}	$IL\pi,\pi^*$
	298	3.4×10^{4}	$IL\pi,\pi^*$
	265	5.0 × 10⁴	$IL\pi,\pi^*$
[(bpy) ₂ (CO)Os''(bpa)Os''(phen)(dppe)Cl] ^{4+ b}	≈1700	$< 2 \times 10^{2}$	$d\pi - d\pi$
	575	1.0×10^{3}	LMCT
	410	3.5×10^{3}	$Os(bpy) \rightarrow bpy MLCT$
	340 (sh)	1.2×10^{4}	$Os(bpy) \rightarrow bpa MLCT$
	310 (sh)	2.5×10^{4}	$\mathrm{IL}\pi,\pi^*$
	298	3.0×10^{4}	$IL\pi,\pi^*$
	265	4.1×10^{4}	$IL\pi,\pi^*$
[(phen)Os ^{III} (dppe)Cl(bpa)] ²⁺	≈1700	$<2 \times 10^{2}$	$d\pi - d\pi$
	580	1.2×10^{3}	LMCT

^aCH₂Cl₂ solvent unless indicated otherwise. ^bSpectrum obtained in CH₃CN/0.1 M TEAP solvent. ^cAbbreviations: MLCT, metal to ligand charge transfer; IL, intraligand π,π^* ; LMCT, ligand to metal charge transfer; $d\pi$ - $d\pi$, metal-center transitions between spin-orbit coupling mixed $d\pi$ levels at Os(III); IT, intervalence transfer.

to values for the associated monomers showing that at best slight resonance and/or electrostatic interactions exist between the two metal centers.⁵

In the bpa-bridged dimer, $E_{1/2}$ values for the three ligand-based reductions (E₁, E₂, E₃ (reductive)) are in agreement with values for the associated monomers [(bpy)₂Os(CO)(bpa)][PF₆]₂ and [(phen)Os(dppe)(Cl)(bpa)][PF₆]. Significantly, a fourth wave appears at $E_{1/2} = -1.29$ V for the 4,4'-bpy dimer. The wave does not appear for either of the corresponding monomers because of the additional electron-withdrawing metal site bound to 4,4'-bpy in the dimer. The ability of the 4,4'-bpy ligand to act as an electron acceptor in the dimer is photochemically significant as we shall see later.

B. UV-Vis Spectral Properties. Monomers and (II,II) Dimers: Figures 1 and 2 depict absorption spectra for the monomers and the dimers (L = bpa and 4,4'-bpy); a summary of the spectral bands is presented in Table II. The dimer absorption spectra are essentially the sum of the absorption spectra of the monomers confirming that the dimers contain at best weakly interacting chromophores.

Mixed Valence (II,III) Dimers: The UV-vis absorption spectrum of the mixed valence dimer $[(bpy)_2Os^{II}(CO)(L)Os^{III}$ -(phen)(dppe)(Cl)]⁴⁺ (L = bpa) generated by electrolytic oxidation of the (II,II) dimer is presented in Figure 3. Compared to the (II,II) dimer, for the (II,III) dimer there is a decrease in absorption in the region 400 nm $< \lambda < 500$ nm due to loss of the $d\pi(Os)$ $\rightarrow \pi^*(phen)MLCT$ absorption band. Also, a weak band appears at $\lambda_{max} = 580$ nm ($\epsilon \sim 1.2 \times 10^3$ M⁻¹ cm⁻¹) which has analogues in the Os(III) monomers and can be assigned to a ligand to metal charge transfer (LMCT) transition localized at [(L)Os^{III}-(phen)(dppe)(Cl)].^{9b}

II,III Dimers: Near-IR Spectra. Near-IR spectra have been obtained on concentrated solutions of the mixed-valence dimers in an attempt to observe the usually weak intervalence transfer (IT) band which corresponds to optically induced electron transfer between the metal centers.^{3b,5} For the 4,4'-bpy-bridged dimer a



Figure 3. Absorption spectra of (II,II) and (II,III) bpa dimers, CH₃CN solvent. (-) $[(bpy)_2(CO)Os^{II}(bpa)Os^{II}(phen)(dppe)(Cl)]^{3+};$ (---), [(bpy)₂(CO)Os^{II}(bpa)Os^{III}(phen)(dppe)(Cl)]⁴⁺.

TABLE III. Emission Energies and Intensities at 300 K

compd	λ_{max} , ^a nm	rel. intens
[(bpy) ₂ Os ^{II} (CO)(4,4'-bpy)] ²⁺	580 (590 ^b)	1.0
$[(phen)Os^{II}(dppe)Cl(4,4'-bpy)]^+$	679	0.19
$[(bpy)_2(CO)Os^{11}(4,4'-bpy)Os^{11}(phen)(dppe)Cl]^{3+}$	с	с
$[(bpy)_2(CO)Os^{II}(4,4'-bpy)Os^{III}(phen)(dppe)Cl]^{4+}$	600 ^b	
$[(bpy)_2Os^{II}(CO)(bpa)]^{2+}$	588 (600 ^b)	0.73
[(phen)Os ^{II} (dppe)Cl(bpa)] ⁺	687	0.16
[(bpy) ₂ (CO)Os ^{II} (bpa)Os ^{II} (phen)(dppe)Cl] ³⁺	688	0.071
[(bpy) ₂ (CO)Os ^{II} (bpa)Os ^{III} (phen)(dppe)Cl] ⁴⁺	607 ^{<i>b</i>}	0.14

^a λ_{max} in CH₂Cl₂ except where indicated. ^b λ_{max} in CH₃CN. ^cNo detectable emission.

broad, weak absorption band is apparent in the region extending from 700 to 1000 nm which is not observed in the corresponding Os(III) monomer, [(phen)Os^{III}(dppe)(Cl)(4,4'-bpy)]²⁺, and can be assigned to the IT transition in eq 3, as observed in related

$$[(bpy)_{2}(CO)Os^{II}(4,4'-bpy)Os^{III}(phen)(dppe)(Cl)]^{4+} \xrightarrow{h\nu} \\ [(bpy)_{2}(CO)Os^{III}(4,4'-bpy)Os^{II}(phen)(dppe)(Cl)]^{4+} (3)$$

mixed-valence ions^{5,18,22} and metal complex ion pairs.¹⁹ Unfortunately, the IT band is partially obscured by the LMCT absorption band at 580 nm which occurs both in the (II,III) dimer and in the corresponding Os(III) monomer. In order to estimate the properties of the IT band, the absorption due to the 580-nm band was subtracted by using the spectrum of the corresponding Os(III) monomer which gave²⁰ $\lambda_{max} = 700 \text{ nm}, \epsilon_{max} = 600 \text{ M}^{-1} \text{ cm}^{-1}$, and for the bandwidth at half-height, $\Delta \nu_{1/2} = 4620 \text{ cm}^{-1}$. The IT band for [(bpy)₂(CO)Os^{II}(4,4'-bpy)Os^{III}(phen)(dppe)-(Cl)]⁴⁺ occurs at a relatively high energy due to the large redox asymmetry,²¹ which as estimated from the redox potentials for the dimer in Table I is $\Delta E \approx E_2 - E_1 = 0.7$ eV. From earlier work on the related symmetrical dimer, [(bpy)₂(Cl)Os^{II}- $(PPh_2CH_2PPh_2)Os^{III}(Cl)(bpy)_2]^{3+}$, we conclude that we are observing the lowest of three IT transitions.^{18d} Three transitions are expected because optical excitation at Os(II) can occur from any of three nondegenerate $d\pi$ orbitals.

We were unable to observe an IT band for the bpa-bridged dimer. Presumably the band exists but is of low intensity because



Figure 4. Emission spectra of $[(phen)Os(dppe)(Cl)(bpa)]^+$ (---) and $[(bpy)_2(CO)Os(bpa)Os(phen)(dppe)(Cl)]^{3+}$ (--) at 77 K in EtOH/ MeOH (4:1), excitation wavelength 400 nm (25000 cm⁻¹).

of weak electronic coupling between the metal sites through the bpa bridging ligand.5b

C. Emission Spectra and Lifetimes. bpa Compounds. Emission spectra for [(bpy)₂(CO)Os(bpa)Os(phen)(dppe)(Cl)]³⁺ and the respective monomers, $[(bpy)_2Os(CO)(bpa)]^{2+}$ and [(phen)Os(dppe)(bpa)(Cl)]⁺, were obtained at room temperature in CH2Cl2; λ_{max} values and relative emission yields are summarized in Table III. The luminescence spectra and lifetimes (Table IV) are consistent with an MLCT assignment for the emitting states in each case.²³ The following features in the data are of interest: (1) The emitting MLCT state of $[(bpy)_2Os(CO)(bpa)]^{2+}$ is approximately 2500 cm⁻¹ higher in energy than for [(phen)Os-(dppe)(Cl)(bpa)]⁺. (2) Emission from the dimer, [(bpy)₂-(CO)Os(bpa)Os(phen)(dppe)(Cl)]³⁺, is superimposable on emission from the "low-energy" monomer, [(phen)Os(dppe)-(Cl)bpa]⁺, except for a weak band which appears on the highenergy side of the major band. (3) The weak high-energy dimer emission band corresponds in energy to emission from $[(bpy)_2Os(CO)(bpa)]^{2+}$. Features 2 and 3 suggest that the dimer luminescence is a sum of emissions from two localized MLCT excited states with the Os(phen) chromophore dominating emission and a small fraction (<10%) of the emission arising from the Os(bpy) chromophore.

Emission lifetime data (Table IV) give further evidence in support of a dual emission but having strikingly different lifetime characteristics. τ_{em} for [(phen)Os(dppe)(Cl)(bpa)]⁺ corresponds closely to $\tau_{\rm em}$ for the bpa dimer monitored at the Os(phen) emission maximum of 660 nm. However, room temperature lifetimes, monitored at 550 nm to follow the Os(bpy) emission, are 1200 ns for $[(bpy)_2Os(CO)bpa]^{2+}$ and <10 ns for the bpa dimer, indicating that emission from the Os(bpy) chromophore in the dimer is strongly quenched.

Emission spectra and lifetimes for the bpa compounds have also been obtained at 77 K in a 4:1 EtOH/MeOH glass. Luminescence spectra of [(bpy)₂(CO)Os(bpa)Os(phen)(dppe)Cl]³⁺ and [(phen)Os(dppe)Cl(bpa)]⁺ at 77 K are reproduced in Figure 4. Once again, the Os(phen)-based luminescence in the dimer is superimposable with the monomer except for a small high-energy component. The lifetime data at 77 K show the same trends noted at room temperature (RT). The low-energy (650 nm) bpa dimer and monomer, [(phen)Os(dppe)Cl(bpa)]⁺, emission lifetimes are in agreement while dimer emission from the high-energy Os(bpy) site (550 nm) has a significantly shorter lifetime than does [(bpy)₂Os(CO)(bpa)]²⁺ (45 and 5430 ns, respectively). Although the photophysical properties of the bpa dimer are similar at 77

^{(18) (}a) Meyer, T. J. Ann. N.Y. Acad. Sci. **1978**, 313, 496. (b) Powers, M. J.; Meyer, J. T. Inorg. Chem. **1978**, 17, 1785. (c) Powers, M. J.; Meyer, T. J. J. Am. Chem. Soc. **1980**, 102, 1289. (d) Kober, E. M.; Goldsby, K. A.; Narayana, D. S.; Meyer, T. J. J. Am. Chem. Soc. **1983**, 105, 4303.

⁽¹⁹⁾ Curtis, J. C.; Meyer, T. J. Inorg. Chem. 1982, 21, 1562.

⁽²⁰⁾ The corrected vis-near-IR spectra of the mixed-valence dimer are available as supplementary material.
(21) Hush, N. S. Prog. Inorg. Chem. 1961, 8, 391.
(22) (a) Goldsby, K. A., Ph.D. Dissertation, University of North Carolina

at Chapel Hill, 1983. (b) Goldsby, K. A.; Meyer, T. J. Inorg. Chem. 1984, 23, 3002.

⁽²³⁾ The photophysical properties of the 2,2'-bipyridine and 1,10phenanthroline substituted Os(II) complexes are similar to those of other well-characterized Os(II) complexes with lowest MLCT excited states, see ref 6c, 9, 12, 16.

TABLE IV. Emission Lifetimes in 4:1 EtOH/MeOH at 77 and 300 K^a

		au,	ns	
compd	$\lambda_{monitor}, nm$	300 K	77 K	
$[(bpy)_{2}(CO)Os^{II}(4,4'-bpy)]^{2+}$	550	1310	5260	
$[(phen)(Cl)Os^{II}(dppe)(4,4'-bpy)]^+$	625	290	4070	
$[(bpy)_2(CO)Os^{II}(4,4'-bpy)Os^{II}(phen)(dppe)(Cl)]^{3+b,c}$	550	d	<10 ^e	
	625	d	3930	
$[(bpy)_2(CO)Os^{II}(4,4'-bpy)Os^{III}(phen)(dppe)(Cl)]^{4+}$	590	1970 ^g		
$[(bpy)_{2}(CO)Os^{II}(bpa)]^{2+}$	550	1200	5430	
$[(phen)(Cl)Os^{II}(dppe)(bpa)]^+$	640	220	3800	
$[(bpy)_2(CO)Os^{II}(bpa)Os^{II}(phen)(dppe)(CI)]^{3+b,c}$	550	<10 ^e	≈45⁄	
	640	160	3740	
$[(bpy)_2(CO)Os^{II}(bpa)Os^{III}(phen)(dppe)(Cl)]^{4+}$		1620 ^g		

^a All lifetimes fit first-order decay kinetics unless otherwise indicated. ^bNote that dual emissions are noted for the dimers (see text). ^cEmission decay monitored t 550 nm does not fit first-order decay kinetics (see text). ^dNo emission at room temperature. ^cLifetime too short for measurement. ^fLifetime calculated as $1/k_1$ from Table VI; see text for more detail. ^gLifetimes measured in CH₃CN/0.1 M TEAP solution.

TABLE V.	Vibrational	Parameters	from	Emission	Spectral	Fitting ^a

compd	$E_{00}, {\rm cm}^{-1}$	$\hbar \omega_{\rm M}$, cm ⁻¹	S _M	$\hbar \omega_{\rm L}, {\rm cm}^{-1}$	SL	$\bar{\nu}_{1/2}, \mathrm{cm}^{-1}$
$[(phen)(Cl)Os^{II}(dpp)(4,4'-bpy)]^+$	16 400	1250	0.90	400	1.65	850
$[(bpy)_2(CO)Os^{II}(4,4'-bpy)]^{2+}$	18770	1275	1.20	400	1.78	800
$[(bpy)_2(CO)Os^{II}(4,4'-bpy)Os^{II}(phen)(dppe)(Cl)]^{3+}$	16 400	1275	0.88	400	1.62	850
[(phen)(Cl)Os ¹ I(dppe)(bpa)] ⁺	16250	1250	0.90	400	1.75	850
$[(bpy)_2(CO)Os^{II}(bpa)]^{2+}$	18625	1275	1.20	400	1.75	800
[(bpy) ₂ (CO)Os ^{II} (bpa)Os ^{II} (phen)(dppe)(Cl)] ³⁺	16 200	1250	0.88	400	1.75	850

^a From spectra at 77 K in a 4:1 EtOH/MeOH glass.

K and RT, at low temperatures we were able to measure the lifetime of the emission from the Os(bpy) localized MLCT state at 550 nm, thus allowing an estimate to be made for the rate of the quenching reaction which rapidly diactivates the state (vide infra).

4,4'-bpy Compounds. As the data in Table III indicate, the 4,4'-bpy monomers, $[(bpy)_2Os(CO)(4,4'-bpy)]^{2+}$ and $[(phen)-Os(dppe)(Cl)(4,4'-bpy)]^+$, display typical MLCT luminescences with λ_{max} values slightly blue-shifted compared to the corresponding bpa complexes. However, a remakable feature is that the corresponding dimer, $[(bpy)_2(CO)Os(4,4'-bpy)Os(phen)-(dppe)Cl]^{3+}$, does not luminesce at room temperature.

Emission spectra and lifetimes for the 4,4'-bpy compounds have also been obtained at 77 K in a 4:1 EtOH/MeOH glass. The emission spectra of the 4,4'-bpy dimer and [(phen)Os(dppe)Cl-(4,4'-bpy)]⁺ are reproduced in Figure 5; the dimer displays a reasonably strong luminescence in the frozen solution. It is evident that the luminescence spectra in the glass are essentially identical. Also noteworthy is the fact that the weak high-energy emission band noted for the bpa dimer is considerably weaker in the spectrum of the 4,4'-bpy-bridged dimer. Furthermore, luminescence lifetimes for the 4,4'-bpy dimer and monomer, [(phen)Os(dppe)Cl(4,4'-bpy)]⁺, are the same within experimental error (Table IV).

The 77 K emission data suggest that luminescence from $[(bpy)_2(CO)Os(4,4'-bpy)Os(phen)(dppe)Cl]^{3+}$ occurs nearly exclusively from an Os(phen) localized MLCT excited state. The fact that very little emission occurs from the MLCT state localized at $[(bpy)_2Os(CO)(L)]$ indicates that excitation of the Os(bpy) chromophore must be followed by an extremely rapid deactivation process $(k > 5 \times 10^8 \text{ s}^{-1})$.

D. Low-Temperature Emission Spectral Fitting. The 77 K emission spectra of the monomers and dimers have been fitted by using a Franck-Condon vibronic band analysis which has been previously described.¹² In the procedure it is assumed that both medium ($\hbar\omega \sim 1300 \text{ cm}^{-1}$) and low ($\sim 400 \text{ cm}^{-1}$) frequency vibrational modes play the dominant role in determining emission band shapes. In the treatment the two modes represent averaged contributions from a series of medium- and low-frequency acceptor vibrations. Parameters obtained from the fits include: the 0,0 energy gap between the excited and ground state, E(0-0), the vibrational frequencies of the medium ($\nu_{\rm M}$) and low frequency ($\nu_{\rm L}$) acceptor vibrational modes, the electron-vibrational coupling constants ($S_{\rm M}$ and $S_{\rm L}$) which are related to the difference in



Figure 5. Emission spectra of $[(phen)Os(dppe)(Cl)(4,4'-bpy)]^+$ (---) and $[(bpy)_2(CO)Os(4,4'-bpy)Os(phen)(dppe)(Cl)]^{3+}$ (--) at 77 K in EtOH/MeOH (4:1), excitation wavelength 400 nm (25000 cm⁻¹).

equilibrium coordinates for a given normal mode between the ground and excited states (ΔQ_e) by $S = \frac{1}{2}(M\omega/\hbar)(\Delta Q_e)^2$ where M is the reduced mass, ω is the angular frequency of the vibration, and $\overline{\nu}_{1/2}$ is the full width at half-maximum of the 0–0 vibrational emission component.

The results of the fits are collected in Table V. In each case the spectra are dominated by a medium-frequency vibrational progression ($\bar{\nu}_{\rm M} = 1200-1350$ cm⁻¹) which on the basis of studies on other Ru(II) and Os(II) polypyridine complexes is assigned to a series of modes largely ν (bpy,phen) ring stretching in character.^{12,24} Although a low-frequency progression ($\nu_{\rm L}$) is not resolved in the spectra, the quality of the fits relies on its inclusion. Noteworthy features in the parameters derived from spectral fittings include (1) the nearly identical parameters for the pairs, [(phen)Os(dppe)(Cl)L]⁺ and [(bpy)₂(CO)Os(L)Os(phen)-(dppe)Cl]³⁺ (L = bpa and 4,4'-bpy), which reinforce the similarity of the emitting states in the dimers and corresponding monomers;

^{(24) (}a) Hager, G. D.; Crosby, G. A. J. Am. Chem. Soc. 1975, 97, 7031.
(b) Casper, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. J. Am. Chem. Soc. 1982, 104, 630. (c) Caspar, J. V.; Meyer, T. J. J. Am. Chem. Soc. 1983, 105, 5583.



Figure 6. Emission spectra of $[(bpy)_2(CO)Os^{II}(bpa)]^{2+}$ (---) and $[(bpy)_2(CO)Os^{II}(bpa)Os^{II}(phen)(dppe)(CI)]^{4+}$ (--) at 25 °C in CH₃CN solvent, excitation wavelength 400 nm (25000 cm⁻¹).

(2) an increase in S_M with increased excited-state energy which has already been noted in the series $[Os(bpy)_n(P_2)_{3-n}]^{2+}$ (n = 1, 2, 3) and has been suggested to indicate a greater degree of M \rightarrow L charge transfer with increased excited-state energy.¹²

E. Emission. Mixed-Valence (II,III) Dimers. The mixedvalence ions, $[(bpy)_2(CO)Os^{II}(L)Os^{III}(phen)(dppe)Cl]^{4+}$ (L = bpa and 4,4'-bpy), emit at room temperature. Figure 6 shows RT emission spectra of the bpa(II,III) dimer and the monomer $[(bpy)_2Os(CO)(bpa)]^{2+}$; the spectra are similar except for a slight red shift in λ_{max} for the mixed-valence ion. The emission lifetime for the bpa(II,III) dimer at RT is slightly longer (1620 ns) than the lifetime of $[(bpy)_2Os(CO)(bpa)]^{2+}$ (1200 ns).

Discussion of the Photophysical Properties of the Os(II)-Os(II) Dimers

A. bpa Dimer. Assignments of the visible-near-UV absorption bands for the unsymmetrical Os(II)-Os(II) dimers are made in Table II. Based on the assignments, photolysis of the dimer at low energy ($\lambda > 500$ nm) should result in selective excitation of the Os(phen) chromophore, and photolysis at higher energy leads to excitation at both the Os(phen) and Os(bpy) MLCT chromophores.

If there were no coupling between the localized MLCT states, irradiation within the 300-500-nm region should result in photophysical properties which are the sum of the properties of the individual MLCT chromophores. That this is not the case is demonstrated by the emission spectral and lifetime results. At 77 K < T < 300 K, emission from the dimer is virtually identical with emission from [(phen)Os(dppe)(Cl)(bpa)]⁺. Regardless of excitation wavelength for the dimer, the predominant emitting state is the localized Os(phen) MLCT state:

The appearance of the weak high-energy shoulder in the emission spectrum at both 77 and 300 K signals a contribution from the higher energy, Os(bpy) localized excited state,

$$[(bpy)(bpy^{-})Os^{II}(bpa)Os^{II}(phen)(dppe)]^{3+*} - - - \\ | | | \\ C C I \\ [(bpy)_2Os^{II}(bpa)Os^{II}(phen)(dppe)]^{3+} + h\nu (5) \\ | | | \\ C C I \end{bmatrix}$$



Figure 7. Transient absorption spectra following 355-nm laser excitation (10 ns fwhm, 10 mJ/pulse), CH_2Cl_2 solvent, 25 °C. (a) $[(bpy)_2(CO)-Os(bpa)]^{2+}$ (--) and $[(phen)Os(dppe)(Cl)(bpa)]^{+}$ (--) at 20-ns delay after excitation pulse. (b) $[(bpy)_2(CO)Os(bpa)Os(phen)(dppe)(Cl)]^{3+}$ at 15-ns delay (--) and 200-ns delay (--) after excitation pulse.

The high-energy emission is remarkably short-lived in the dimer. In the monomer, $[(bpy)_2Os^{II}(CO)(bpa)]^{2+}$, the lifetimes are $\tau(77 \text{ K}) = 5430 \text{ ns}$ and $\tau(300 \text{ K}) = 1200 \text{ ns}$, while for the same chromophore in the dimer the lifetimes are $\tau(77 \text{ K}) = 35 \text{ ns}$ and $\tau(300 \text{ K}) < 10 \text{ ns}$. Apparently, the Os(bpy) localized excited state in the dimer is populated by optical excitation, but is deactivated very rapidly by an intramolecular quenching process which is not available to the monomer. The shortened lifetime but appropriate λ_{max} for Os(bpy) emission provides strong evidence that the emission is intrinsic to the dimer and not from a monomer impurity.

Nanosecond time-resolved transient absorption spectra of $[(bpy)_2Os^{II}(CO)(bpa)]^{2+}$, $[(phen)Os^{II}(dppe)(CI)(bpa)]^+$, and $[(bpy)_2(CO)Os^{II}(bpa)Os^{II}(phen)(dppe)(CI)]^{3+}$ give additional evidence that the high-energy MLCT excited state in the dimer, $[(bpy)(bpy^{-})Os^{III}(CO)(bpa)Os^{II}(phen)(dppe)(CI)]^{3+*}$, is formed via excitation but is rapidly quenched. Figure 7 shows difference spectra (following a 10-ns, 355-nm laser pulse) for the monomeric compounds at 300 K in CH₂Cl₂ and of the dimer at 100 K in 4:1

EtOH/MeOH (solvent glass), respectively. The absorption changes noted for the dimer immediately after the laser pulse are apparently a composite of the transient spectra of the two monomeric analogues. Following the flash, two excited dimeric species are present as expected for the localized MLCT excited states [(bpy)(bpy⁻)(CO)Os^{III}(bpa)Os^{II}(phen)(dppe)(Cl)]^{3+*} and [(bpy)₂(CO)Os^{II}(bpa)Os^{III}(phen⁻)(dppe)Cl]^{3+*}. However, the difference spectrum for the dimer evolves rapidly (within 200 ns at 100 K) into a spectrum which is basically the same as the difference spectrum for photoexcited [(phen)Os(dppe)(Cl)(bpa)]⁺. Decay of the short-lived transient occurs with $\tau \approx 30$ ns (at 100 K) which is nearly identical with the lifetime of the Os(bpy)centered emission in [(bpy)(bpy⁻)(CO)Os^{III}(bpa)Os^{II}(phen)-(dppe)Cl]^{3+*} at 77 K. The transient absorption changes observed for the dimer with $\tau \approx 30$ ns appear to arise from decay of the locally excited Os(bpy) MLCT state.

For the bpa dimer the following catalogue of photophysical events are consistent with our experimental observations: (1) Immediately following the excitation pulse both $d\pi(Os) \rightarrow \pi^*$ -(bpy) and $d\pi(Os) \rightarrow \pi^*(phen)$ excited states are present, [(bpy)(bpy')(CO)Os^{III}(bpa)Os^{III}(phen)(dppe)(Cl)]^{3+*} and $[(bpy)_2(CO)Os^{II}(bpa)Os^{III}(phen')(dppe)(Cl)]^{3+*}$. (2) The higher energy state, [(bpy)(bpy⁻)(CO)Os^{III}(bpa)Os^{II}(phen)(dppe)Cl]^{3+*}, decays far more rapidly in the dimer than in the associated monomer, $[(bpy)(bpy^{-})Os^{III}(CO)(bpy)]^{2+*}$. (3) When the Os-(bpy)-based MLCT state decays, only the low-energy state, $[(bpy)_2(CO)Os^{II}(bpa)Os^{III}(phen^-)(CI)]^{3+*}$, is observed. (4) The decay characteristics of the Os(phen) MLCT state are the same as for the MLCT state of [(phen)Os^{II}(dppe)(Cl)(bpa)]⁺.

The important question is how the Os(bpy) localized excited state is quenched in the bpa-bridged dimer. One possibility is decay via direct, intramolecular energy transfer between the Os(bpy) and Os(phen) MLCT chromophores:

The energy change for this process can be estimated as -0.30 eV from the difference in MLCT emission energies for [(bpy)₂Os-(CO)(bpa)]²⁺ and [(phen)Os(dppe)(Cl)(bpa)]⁺. Exothermic excited-state energy transfer in organic²⁵ and some inorganic systems⁷ is known to be rapid. The two excited states are expected to be largely "triplet" in character²⁷ so that electronic energy transfer might be expected to be dominated by the Dexter exchange mechanism which requires oribtal overlap between the donor and acceptor groups.²⁸ Given the absorption and emission characteristics of the acceptor and donor, Franck-Condon factors for energy transfer are expected to be relatively high²⁹ and if electronic coupling is sufficient it is expected that energy transfer should be rapid.26

Energy transfer necessarily involves the population of the Os(phen)-based state concomitant with Os(bpy) localized excited-state decay. Thus, the excitation spectrum for the Os(phen) emission should show bands characteristic of both chromophores if energy transfer is a significant process. Corrected excitation spectra for the dimer emission monitored at the maximum for the



Figure 8. Corrected and normalized excitation spectra for bpa complexes at room temperature in CH_2Cl_2 . [(bpy)₂(CO)Os(bpa)]²⁺ (-...-), emission monitored at 550 nm; [(phen)Os(dppe)(Cl)(bpa)]⁺ (-) and [(bpy)₂(CO)Os(bpa)Os(phen)(dppe)(Cl)]³⁺ (---), emission monitored at 650 nm.

SCHEME I



Os(phen) emission have been obtained as shown in Figure 8 which also depicts excitation spectra for the corresponding monomers. It is apparent from the figure that the Os(bpy) chromphore does not sensitize the Os(phen) emission to any significant degree; the excitation spectrum for the Os(phen) localized excited state in the dimer is virtually identical with the excitation spectrum of [(phen)Os(dppe)(Cl)(bpa)]⁺. An important feature is that the strong excitation band present in $[(bpy)_2Os(CO)(bpa)]^{2+}$ at 320-340 nm is not present in the excitation spectrum for the low-energy dimer luminescence. We are forced to conclude that quenching of the higher energy, Os(bpy) localized excited state in the dimer does not occur to any significant extent by energy transfer, at least to the emitting Os(phen) localized MLCT excited state.

An alternate quenching mechanism would be by an intramolecular electron-transfer step from the adjacent Os^{II}(phen) center

From appropriate redox potentials and the excited-state energy we calculate that the intramolecular quenching reaction in eq 7 is spontaneous or nearly spontaneous. When the ground-state potentials for reduction at the Os(bpy) center (-1.12 V) and oxidation of the Os(phen) center (+0.93 V) along with the Os^{III}(bpy⁻⁻) excited-state energy (2.11 eV) are used,³¹ the free energy change which accompanies the electron transfer in eq 7 is slightly exergonic ($\Delta G \simeq -0.05 \text{ eV}$), neglecting electrostatic work term differences.

^{(25) (}a) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin-Cummings: Menlo Park, CA, 1978; Chapter 9. (b) Lamola, A. A. "Energy Transfer and Organic Photochemistry"; Lamola, A. A., and Turro, N. J., Eds.; Interscience: New York, 1969; p 17.

⁽²⁶⁾ Gandolfi, M. T.; Maestri, M.; Sandrini, D.; Balzani, V. Inorg. Chem. **1983**, 22, 3435. (27) Kober, E. M.; Meyer, T. J. Inorg. Chem. **1984**, 23, 3877.

⁽²⁸⁾ Dexter, D. L. J. Chem. Phys. 1953, 21, 836.
(29) The Franck-Condon factor for energy transfer in this system was calculated to be ≥ 0.3 by using a method similar to that described by Balzani et al., see ref 30

⁽³⁰⁾ Orlandi, G.; Monti, S.; Barigelletti, F.; Balzani, V. Chem. Phys. 1980, 52, 313.

⁽³¹⁾ Redox potentials and excited state energies in CH₃CN solvent. (32) Rehm, D.; Weller, A. Isr. J. Chem. 1970, 8, 259.

TABLE VI. Rate Constants for the Excited-State Decay of $[(bpy)_2(CO)Os(bpa)Os(phen)(dppe)(Cl)]^{3+}$ in 4:1 EtOH/MeOH (See Scheme I)^a

	rate const $\times 10^{-7}$ s ⁻¹					
Т, К	$\overline{k_1}$	k ₂	<i>k</i> ₃	k_4		
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		

^aThe values of k_4 were obtained from emission lifetimes of $[(bpy)_2Os(CO)(bpa)]^{2+}$.

An important point is that the intramolecular quenching step in eq 7 would correspond to electron transfer within a photochemically prepared mixed-valence dimer $Os^{III}-L-Os^{II}$. The excited-state mixed-valence dimer is generated following initial MLCT excitation of the Os(bpy) chromophore. With this interpretation, the rate of disappearence of [(bpy)(bpy⁻)(CO)-Os^{III}(bpa)Os^{II}(phen)(dppe)(CI)]^{3+*} gives a direct measure of the rate of intramolecular electron transfer within the photogenerated mixed-valence dimer.⁸

A general kinetic scheme assuming that intramolecular electron transfer quenching does occur is shown in Scheme I. From the general integrated rate law for Scheme I, 1d,33 decay of the intermediate, [(bpy)(bpy⁻)(CO)Os^{III}(bpa)Os^{II}(phen)(dppe)-(Cl)]^{3+*}, should follow nonexponential kinetics. Time-resolved emission data for the (bpy⁻)Os^{III} state at 550 nm were obtained over the 77–160 K temperature range. The decay data do not follow single-exponential, first-order kinetics. Rather, a triple-exponential expression, eq 8, was required to obtain reasonable

$$I(t) = Ae^{-m_1 t} + Be^{-m_2 t} + Ce^{-m_3 t}$$
(8)

fits to the experimental data. From the fits, it is obvious that a small fraction of the total intensity decay occurs by a relatively slow process (long lifetime) which can be ascribed to trace amounts of a monomeric impurity or to a contribution from emission by the Os(phen) site at 550 nm. The majority (>92%) of the decay profile at all temperatures arises from the components m_1 and m_2 in eq 8. Based on a method described in the literature^{1d} the parameters obtained from the multiexponential fits were used to calculate the rate constants in Table VI. The rate constants pertain to the processes shown in Scheme I.³⁴

The kinetic events proposed in Scheme I are at least consistent with the decay kinetics although we have no definitive evidence that quenching actually occurs by intramolecular electron transfer. Assuming that it does, k_1 and k_2 are respectively the rates for forward and reverse electron transfer within the mixed-valence, excited-state dimer, $[(bpy)(bpy^-)(CO)Os^{III}(bpa)Os^{II}(phen)-(dppe)(CI)]^{3+*}$. The data in Table VI show that k_1 is relatively temperature independent up to the glass to fluid transition temperature of the solvent. Above the glass to fluid transition, the rate becomes too fast to measure with our apparatus. The enhancement in rate at the glass to fluid transition suggests that there is a contribution to electron trapping in the rigid medium arising from the nonequilibrium, "frozen" orientational polarization of the solvent dipoles.

An interesting feature of the proposed intramolecular quenching step is that it would produce a charge separated, "remote" MLCT excited state, [(bpy)(bpy^{.-})Os^{II}(bpa)Os^{III}(phen)(dppe)(Cl)]³⁺, in which the electron-hole pair is separated by the intervening Os^{II} center and the bpa-bridging ligand. Production of a "remote" SCHEME II



MLCT excited state is interesting in that it raises the possibility of providing a basis for relatively long-lived intramolecular charge storage given the relative isolation of the oxidized and reduced sites. Although we have been unable to obtain direct spectroscopic evidence for the remote MLCT state,³⁵ analysis of emission decay for [(bpy)(bpy⁻)(CO)Os^{III}(bpa)Os^{II}(phen)(dppe)(CI)]^{3+*} based on the kinetic model in Scheme I gives an estimated value for its rate of decay, k_3 , in Table VI. It is clear that even at low temperatures, decay of the state is disappointingly rapid ($k - 10^7 \text{ s}^{-1}$, $\tau \sim 100 \text{ ns}$), indicating that, suprisingly, the remote MLCT state is relatively short-lived. A possible basis for excited-state decay is in the rotationally flexible nature of the bpa ligand through the $-CH_2CH_2$ - link. Rotational reorientations at the link could allow through-space contact between the bpy⁻ and Os^{III} sites and decay by outer-sphere electron transfer.

The important features regarding the photophysics of the bpy dimer are summarized in the Jablonski-type diagram in Scheme II. Notable characteristics include the following: (1) The lowest energy MLCT state of the dimer is Os^{III}(phen⁻) based and the properties of this localized state are unperturbed by the nearby Os(bpy) center. (2) The high-energy, Os^{III}(bpy⁻) MLCT state is rapidly deactivated. (3) The Os^{III}(bpy⁻) MLCT excited state does not sensitize the Os^{III}(phen⁻) MLCT state by direct or indirect energy transfer to any significant degree. (4) A likely quenching pathway is by intramolecular electron transfer from the adjacent Os^{II}(phen) site.

B. 4,4'-bpy-Bridged Dimer. The photophysics of the 4,4'bpy-bridged dimer system at low temperatures (in a 4:1 EtOH/MeOH glass) are very similar to the photophysics of the bpa-bridged dimer. The emission spectrum and lifetime data (Figure 5 and Table IV) show that the dominant emission can be assigned to MLCT luminescence from the Os(phen) localized state, [(bpy)₂(CO)Os^{II}(4,4'-bpy)Os^{III}(phen'⁻)(dppe)(Cl)]^{3+*}. One notable difference is the fact that the weak emission attributable to the high-energy MLCT state, [(bpy)(bpy')(CO)Os^{III}(4,4'bpy)Os^{II}(phen)(dppe)(Cl)]^{3+*}, is $\approx 1/10$ as intense in the 4,4'-bpy dimer relative to the analogous emission in the bpa dimer and is short-lived ($\tau < 10$ ns at 77 K) suggesting that intramolecular quenching is even more rapid for the dimer with 4,4'-bpy as the bridging ligand. Energy transfer from Os^{III}(bpy⁻) to Os^{III}(phen⁻) as a quenching mechanism can be ruled out on the basis of excitation spectra which show that the Os(bpy) chromophore does not sensitize emission from the Os(phen) state. Once again, a reasonable explanation is that quenching occurs by intramolecular electron transfer, eq 9.

As noted above, the available photophysical information indicates that intramolecular excited-state electron transfer is more rapid for the 4,4'-bpy-bridged dimer. Given the similarities in molecular and electronic structure between the two dimers, if intramolecular electron transfer does occur, a factor that may play a role in the enhanced rate for the 4,4'-bpy dimer is that electronic

⁽³³⁾ Zachariasse, K. A.; Kuhnle, W.; Weller, A. Chem. Phys. Lett. 1978, 59, 375.

⁽³⁴⁾ The following are available as supplementary material: (1) a detailed outline of the method used for calculation of the rate constants in Table VI from the experimental fits; (2) a table of the calculated fitting parameters.

⁽³⁵⁾ Careful analysis of the transient absorbance spectral data for the bpa dimer indicates that strong absorption due to the "remote" MLCT state is not observed after excitation; presumably at any given time only a small concentration of this state is present due to its rapid decay rate, see Scheme I.

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coupling between the metal centers is greater.⁴⁶ This premise is supported by the appearance of an intervalence transfer absorption band for the dimer, $[(bpy)_2(CO)Os^{II}(4,4'-bpy)Os^{III}(phen)-(dppe)Cl]^{4+}$ ($\lambda_{max} = 750-800$ nm, $\epsilon = 600$ M⁻¹ cm⁻¹), and the absence of a band for the bpa-bridged dimer ($\epsilon \le 50$ M⁻¹ cm⁻¹).²¹

All available evidence points to the fact that the low-temperature frozen matrix photophysical properties of the two dimers are adequately summarized by the series of processes shown in Scheme II with perhaps the only notable difference between the two being the fact that intramolecular quenching is more rapid for L = 4,4'-bpy. However, the two dimers differ in that the characteristic emission from the lower, Os(phen) localized MLCT state [(bpy)₂(CO)Os^{II}(4,4'-bpy)Os^{III}(phen⁻)(dppe)(Cl)]^{3+*} is quenched at temperatures above the glass to fluid transition in the solvent (T_g , 130–150 K for 4:1 EtOH/MeOH) suggesting that an additional decay mechanism for the Os(phen)-based state must exist for the 4,4'-bpy dimer. The fact that the quenching process does not occur in the bpa dimer or in any of the monomers suggests that the origin of the quenching may lie in the doubly coordinated 4,4'-bipyridine bridging ligand.

Comparison of the transient absorption spectra of the 4,4'-bpy dimer at 100 K (below T_g) and at 300 K, Figure 9, shows conclusively that the nature of the dominant excited state observed after excitation changes dramatically with temperature. Below T_{g} the transient absorption spectrum is similar to the spectrum of the Os(phen) monomer, [(phen)Os(dppe)(Cl)(bpa)]⁺ (compare Figure 7), indicating that in the frozen matrix the dominant excited state for the dimer is [(bpy)₂(CO)Os^{II}(4,4'-bpy)Os^{III}(phen⁻)-(dppe)(Cl)^{3+*}. The transient absorption spectrum obtained at room temperature has the spectral characteristics expected for a $d\pi Os(phen) \rightarrow \pi^*(4,4'-bpy)$ excited state suggesting that at room temperature the excited state reached is [(bpy)₂(CO)-Os^{II}(4,4'-bpy')Os^{III}(phen)(dppe)(Cl)]^{3+*}. The transient absorption spectrum of the state is virtually identical with transient spectra obtained for a family of chromophore-quencher complexes containing the oxidative quencher monoquat

e.g., $[(bpy)_2(CO)Os^{II}(MQ)]^{3+}$ and $[(bpy)Re^{I}(CO)_3(MQ)]^{2+.36}$. In these complexes, the lowest excited state in fluid solution is based upon the MQ⁺ ligand, e.g., $[(bpy)_2(CO)Os^{III}(MQ)]^{3+*}.^{36,37}$. In both the dimer and the chromophore–quencher complexes the intense, low-energy transient absorption bands arise from the pyridinium radical-like character of the excited states.³⁸

The electrochemical data are revealing as to the relative ordering of the MLCT states in the 4,4'-bpy dimer. The data in Table I show that the potentials for reduction of the 4,4'-bpy and phen ligands occur at -1.29 and -1.45 V, respectively, in the dimer. The greater ease of reduction of the 4,4'-bpy bridging ligand compared to the phen ligand suggests that the Os^{II}(phen) \rightarrow 4,4'-bpy MLCT transition would occur at a lower energy than the Os^{II} \rightarrow phen MLCT transition. One point of note is that there is a critical difference between the optical absorption and elec-



Figure 9. Transient absorption spectra at 20-ns delay following 355-nm laser excitation (10 ns fwhm, 10 mJ/pulse) for $[(bpy)_2(CO)Os(4,4'-bpy)Os(phen)(dppe)(Cl)]^{3+}$ in EtOH/MeOH (4:1): (A) 100 K and (B) 25 °C.

trochemical experiments. As for other biphenyl-like molecules, it is expected that the pyridyl rings will be twisted away from coplanarity due to steric effects^{40a} while after addition of an electron, the rings become more nearly planar, to maximize electronic delocalization.^{40b} Because of the Franck–Condon nature of the transition, the energy of the optical excitation to the bridging ligand, Os^{II}(phen) $\frac{h\nu}{}$ Os^{III}(4,4'-bpy⁻), includes an energy contribution from the noncoplanarity of the rings. On the other hand, the electrochemical experiment is a thermodynamic measurement which reflects the relative oxidizing strengths of the phen and equilibrated, flattened (4,4'-bpy) ligand.

The change in equilibrium structure between the (4,4'-bpy) and (4,4'-bpy⁻) ligands also appears to play a major role in the glass

⁽³⁶⁾ Westmoreland, T. D. Ph.D. Dissertation, University of North Carolina at Chapel Hill, 1985.

^{(37) (}a) Westmoreland, T. D.; LeBozec, H.; Murray, R. W.; Meyer, T. J. J. Am. Chem. Soc. 1983, 105, 5952.
(b) Sullivan, B. P.; Abruna, H.; Finklea, H. O.; Salmon, D. J.; Nagle, J. K.; Meyer, T. J., Sprintschnik, Chem. Phys. Lett. 1978, 58, 389.

⁽³⁸⁾ The transient absorbance spectrum of the dimer looks remarkably similar to the absorption spectrum of reduced N,N'-dimethyl-4,4'-bipyridinium ion, see ref 39.

⁽³⁹⁾ Gruver, G. A.; Kuwana, T. J. Electroanal. Chem. 1972, 36, 85.

^{(40) (}a) Suzuki, H. "Electronic Absorption Spectra and Geometry of Organic Molecules"; Academic: New York, 1967. (b) Sullivan, P. D.; Fong, J. Y. Chem. Phys. Lett. 1976, 38, 555.

to fluid induced transition between phen and 4.4'-bpy-localized states. As suggested above, in the ground state the preferred conformation of the 4,4'-bpy bridging ligand is expected to be twisted, while following optical excitation the bridging ligand in the Os(phen) \rightarrow 4,4'-bpy MLCT excited state is expected to adopt the flattened configuration.40b

A question still remains concerning the fate of the upper excited states following excitation. In fluid solution the only state observable following 355-nm excitation is the lowest MLCT state, $[(bpy)_2(CO)Os^{II}(4,4'-bpy'')Os^{III}(phen)(dppe)(Cl)]^{3+*}$, despite the fact that 355-nm excitation also populates states based upon the $[(bpy)_2(CO)Os^{II}]$ site. As noted before, the Os(bpy) states are deactivated extremely rapidly ($k \ge 10^9 \text{ s}^{-1}$), apparently by intramolecular electron-transfer quenching. One possibility is that the upper MLCT states "sensitize" the lowest 4,4'-bpy-based MLCT state indirectly via a series of intramolecular electron- or energy-transfer events as in

 $[(bpy)(bpy^{-})(CO)Os^{III}(4,4'-bpy)Os^{II}(phen)(dppe)(Cl)]^{3+*} \rightarrow$ $[(bpy)(bpy^{-})(CO)Os^{II}(4,4'-bpy)Os^{III}(phen)(dppe)(Cl)]^{3+*}$ (10)

$$[(bpy)(bpy^{-})(CO)Os^{II}(4,4'-bpy)Os^{III}(phen)(dppe)(Cl)]^{3+*} \rightarrow [(bpy)_2(CO)Os^{II}(4,4'-bpy^{-})Os^{III}(phen)(dppe)(Cl)]^{3+*} (11)$$

We have measured the relative efficiencies of formation of [(bpy)₂(CO)Os^{II}(4,4'-bpy'⁻)Os^{III}(phen)(dppe)(Cl)]^{3+*} resulting from both 532- and 355-nm excitation pulses. A graph of absorption due to this excited state vs. laser excitation intensity at the two exciting wavelengths shows that the transient is formed nearly as efficiently following either 355- or 532-nm excitation.⁴¹ The fact that the efficiency of formation of the transient is not strongly affected by excitation energy indicates that upper states such as those in eq 10 and 11 sensitize the formation of the lowest MLCT state with high efficiency compared to direct decay to the ground state. The origin of the intramolecular sensitization may lie in processes such as those shown in eq 10 and 11. However, we cannot rule out intramolecular energy transfer, (bpy -)- $Os^{III}(4,4'-bpy)Os^{II}(phen) \rightarrow (bpy)Os^{II}(4,4'-bpy)Os^{III}(phen^{-1})$ followed by phen \rightarrow 4-4'-bpy electron transfer. Energy transfer across the bridging ligand does not occur to any significant extent below the glass point in 4:1 EtOH-MeOH, but could become more facile in fluid solution if its rate is enhanced by a now allowed flattening of the 4,4'-bpy ligand.

Discussion of the Photophysics of Mixed-Valence Dimers

Because of the large redox asymmetry inherent in the Os-Os dimers, selective one-electron oxidation of the Os^{II}(phen) center can occur giving the mixed-valence dimers, [(bpy)₂(CO)Os^{II}-(L)Os^{III}(phen)(dppe)(Cl)]⁴⁺. In these dimers low-energy absorption is dominated by MLCT transitions at Os^{II}(bpy) (see Figure 3):

$$[(bpy)_{2}(CO)Os^{II}(L)Os^{III}(phen)(dppe)(Cl)]^{4+} \xrightarrow{n\nu} [(bpy)(bpy^{-})(CO)Os^{III}(L)Os^{III}(phen)(dppe)(Cl)]^{4+*} (12)$$

In principle, a number of decay channels are available following Os(bpy) excitation: (1) "Energy transfer" to give the Os^{III}(phen⁻⁻) excited state,

$$[(bpy)(bpy^{-})(CO)Os^{III}(L)Os^{III}(phen)(dppe)(Cl)]^{4+*} \rightarrow [(bpy)_2(CO)Os^{III}(L)Os^{III}(phen^{-})(dppe)(Cl)]^{4+*} (13)$$

(2) Oxidative electron-transfer quenching by the adjacent Os^{III}(phen) site

$$[(bpy)(bpy^{-})(CO)Os^{III}(L)Os^{III}(phen)(dppe)(Cl)]^{4**} \rightarrow [(bpy)_2(CO)Os^{III}(L)Os^{II}(phen)(dppe)(Cl)]^{4+} (14)$$

(3) Normal radiative and nonradiative excited-state decay from the Os^{III}(bpy⁻) localized MLCT state.

$$[(bpy)(bpy^{-})(CO)Os^{III}(L)Os^{III}(phen)(dppe)(Cl)]^{4+*} \rightarrow [(bpy)_2(CO)Os^{II}(L)Os^{III}(phen)(dppe)(Cl)]^{4+} (15)$$

Emission spectra and emission decay lifetimes for the mixedvalence dimers have been obtained (Table IV and Figure 6). For both of the dimers there is a reasonable correspondence between λ_{max} and τ_{em} values for the mixed-valence dimers, $[(bpy)_2(CO)-OS^{II}(L)OS^{II}(phen)(dppe)(Cl)]^{4+}$, and the monomers, $[(bpy)_2-(CO)OS^{II}(L)]^{2+}$. The similarity suggests that the localized (bpy -)Os^{III} excited state is not quenched by intramolecular energy or electron transfer and that the Os(bpy) MLCT state decays via the usual radiative and nonradiative channels characteristic of the monomer. Given the relatively large distance over which an electron must transfer in such quenching processes, it is not surprising that they are slow.⁴⁷ In either case (e.g., eq 13 and 14), electron transfer must occur from (bpy⁻) through Os^{III} and an intervening ligand bridge.

The relative emission quantum yield for [(bpy)₂(CO)Os^{II}-(bpa)Os^{III}(phen)(dppe)(Cl)]⁴⁺ has also been determined, see Table III. Interestingly, the emission yield is approximately 5 times less than for the monomer, $[(bpy)_2(CO)Os^{II}(bpa)]^{2+}$. This decrease in emission yield cannot be ascribed to quenching of the relaxed MLCT excited state since its lifetime (\sim 1700 ns) is not unusually low and is, in fact, predicted for an excited state of this type based upon energy gap law considerations.^{6c,42} One possible explanation for the suppressed emission intensity is that a short-lived, upper excited state is rapidly quenched in competition with its decay to form the luminescent Os^{III}(bpy -) MLCT state. This hypothesis is not unreasonable in light of the results presented above which demonstrate the existence of a complex manifold of MLCT excited states in the unsymmetrical Os dimers. An interesting possibility is that significant quenching occurs from initially populated MLCT singlet states in competition with conversion to lower states largely triplet in character.



Conclusions

The work presented herein provides a basis for understanding the photophysics (and photochemistry) of transition-metal complexes which contain a complicated manifold of electronic excited states. Some of the more important features which were addressed by this study are summarized below:

A. Energy Transfer vs. Electron Transfer. For both the bpa dimer and the 4,4'-bpy dimer (in a frozen matrix) direct energy transfer between the localized MLCT excited states across the ligand bridge is not a competitive process. Facile energy transfer has been observed in a variety of organic biochromophoric systems

⁽⁴¹⁾ The net quantum yield for formation of the 4,4'-bpy-based excited state is estimated as ≥ 0.5 from laser flash photolysis experiments.

 ⁽⁴²⁾ Caspar, J. V.; Meyer, T. J. J. Phys. Chem. 1983, 87, 952.
 (43) Ulstrup, J.; Jortner, J. J. Chem. Phys. 1975, 63, 4358.

⁽⁴⁴⁾ Förster, T. Z. Elektrochem. 1949, 53, 93.

⁽⁴⁵⁾ Alberty, R. A.; Miller, W. G. J. Chem. Phys. 1957, 26, 1231.

⁽⁴⁶⁾ In the weak electronic coupling limit where the frequency for electron transfer is slow compared to the frequency of vibrational equilibration for the trapping vibrations, the preexponential term for electron transfer is predicted to vary as the square of the electronic coupling term, V.

⁽⁴⁷⁾ Miller, J. R.; Beitz, J. V.; Huddleston, R. K. J. Am. Chem. Soc. 1984, 106, 5057 and references therein.

in which singlet-singlet or triplet-triplet energy transfer is favorable with respect to vibrational overlap (Franck-Condon) terms. In the Os dimers, calculations show that the vibrational overlap requirements are very favorable for direct energy transfer²⁹ and given the mixed spin character of the states because of spin-orbit coupling²⁷, either dipole-dipole⁴⁴ (singlet-singlet) or exchange²⁸ (triplet-triplet) interactions are available for electronic coupling. From the kinetic results on the bpa dimer at low temperatures, we can infer that an upper limit for the rate of intramolecular energy transfer is on the order of 10^7 s^{-1} . This rate is surprisingly low despite the large Franck-Condon factors²⁹ and suggests that the energy-transfer process may be inhibited because of weak electronic or dipole-dipole coupling. This hypothesis is supported by experiments with other transition-metal complexes which display relatively inefficient energy transfer.²⁶

B. Electron Transfer in Photoexcited II, II and II, III Dimers. Rapid decay of the Os(bpy) localized excited state in the II,II dimers may occur by intramolecular electron transfer which is sufficiently rapid that it dominates decay by energy transfer. While direct evidence is unavailable to support the suggestion of the electron-transfer quenching, the observed quenching rates are similar to electron-transfer rates in systems with similar separation distances and driving forces.² On the other hand, intramolecular electron-transfer quenching is not an important event for quenching of the Os(bpy) localized excited state in the mixed-valence dimers, [(bpy)(bpy⁻⁾)(CO)Os^{III}(L)Os^{III}(phen)(dppe)(Cl)]⁴⁺. Several factors could be responsible for the apparent lack of quenching by the nearby Os^{III} center. This oxidative electron-transfer reaction is highly exergonic ($\Delta G \sim -1.4 \text{ eV}$), falls in the inverted free energy region,⁴³ and is subject to the vibrational overlap considerations associated with the energy gap law. The rate of electron-transfer quenching may also be strongly affected by the relatively large distance between the bipyridine-localized electron and the Os^{III}(phen) acceptor site. A similar observation has been made in the unsymmetrical mixed-valence Ru dimer, $[(NH_3)_5Ru^{III}(4,4'-bpy)Ru^{II}Cl(bpy)_2]^{4+}$, where following excitation into the $Ru^{II} \rightarrow bpy$ chromophore there is no evidence for significant intramolecular electron transfer quenching via

$$[(NH_{3})_{5}Ru^{III}(4,4'-bpy)Ru^{III}(bpy)(bpy^{-})Cl]^{4+} \rightarrow [(NH_{3})_{5}Ru^{II}(4,4'-bpy)Ru^{III}(bpy)_{2}Cl]^{4+}$$

during the lifetime of the Ru-bpy MLCT excited state.³

C. 4,4'-Bipyridine as a Unique Bridging Ligand. Studies with the 4,4'-bipyridine-bridged dimer show conclusively that the ability of this ligand to act as an electron acceptor is dramatically affected by its conformation. In frozen solution, the ligand is unable to adopt a planar conformation, its ability to act as an electron acceptor is greatly reduced, and the photophysics of the dimer are much the same as in the bpa-bridged dimer. However, in fluid solution the bipyridine rings are free to become planar after accepting an electron and, as a result, the ligand acts as an extremely efficient electron trap.

Due to the fact that the 4,4²-bipyridine ligand is twisted in the ground state, Franck-Condon restrictions prevent direct population

of the bridge-based state via photoexcitation. The fact that formation of the 4,4'-bpy-based state is essentially complete on the timescale of our transient experiments (10 ns) in fluid solution suggests that net intramolecular energy transfer from the Os^{III}-(bpy⁻) and Os^{III}(phen⁻) states to the 4,4'-bpy-based state can occur either by direct energy transfer or by a sequence of 1-electron-transfer steps.

D. Fate of the Remote MLCT Excited State. The results presented suggest that the dominating decay pathway for the Os(bpy) excited state in the bpa dimer system is via an intramolecular electron-transfer reaction which, by inference, would lead to formation of a remote MLCT excited state. Unfortunately we have been unable to monitor this hypothetical state spectroscopically and are forced to conclude that its decay is quite rapid. The rapid decay is a curious feature as this process, (bpy -)- $Os^{II}(bpa)Os^{III}(phen) \rightarrow (bpy)Os^{II}(bpa)Os^{II}(phen)$, involves a rather exothermic charge recombination which should be relatively slow due to Franck-Condon terms and involves electron transfer over a considerable distance. There is also the absence of intramolecular quenching in the structurally similar, mixed-valence MLCT excited states, [(bpy)(bpy -)(CO)Os^{III}(L)Os^{III}Cl-(phen)(dppe)(Cl)]^{4+*}, where the electron-transfer distance is comparable and simply involves an Os(III) component of the bridge between redox sites rather than Os(II). At this point we can only speculate that another excited state may act to mediate the rapid decay of the remote MLCT excited state or that the rotationally flexible nature of the bridging ligand for L = bpa mayplay a role. Further experiments are planned to investigate in more detail the kinetics of formation and decay of these interesting charge separated excited states.

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Registry No. $[(bpy)_2Os(CO)(4,4'-bpy)][PF_6]_2$, 96503-61-6; $[(bpy)_2Os(CO)(bpa)][PF_6]_2$, 96503-65-0; $[(phen)Os(dppe)(Cl)(4,4'-by)][PF_6]$, 96503-63-8; $[(phen)Os(dppe)(Cl)(dpa)][PF_6]_3$, 96532-43-3; $[(bpy)_2(CO)Os(4,4'-bpy)Os(phen)(dppe)(Cl)][PF_6]_3$, 96532-43-7; $[(bpy)_2(CO)Os(bpa)Os(phen)(dppe)(Cl)][PF_6]_3$, 96532-41-1; $[(bpy)_2Os(CO)(CF_3SO_3)][CF_3SO_3]$, 89689-72-5; Os(phen)Cl4, 89689-84-9; $[NH_4]_2[OsCl_6]$, 12125-08-5; *cis*-(phen)Os(dppe)Cl_2, 10093-61-1; $[(bpy)_2(CO)Os(bpa)Os(phen)(dppe)Cl]^{4+}$, 100993-62-2; $[(bpy)_2(CO)-Os(4,4'-bpy)Os(phen)(dppe)Cl]^{4+}$, 100993-63-3; $[(phen)Os(dppe)Cl-(4,4'-bpy)]^{2+}$, 101009-53-4; $[(phen)Os(dppe)Cl(bpa)]^{2+}$, 101009-54-5.

Supplementary Material Available: (1) A table of emission decay parameters based on eq 8 for $[(bpy)_2(CO)Os^{II}(bpa)Os^{II}(phen)(dppe)Cl]^{3+}$, (2) a detailed outline of the method of calculation of the rate constants in Table VI from the experimental data, (3) calculated intervalence transfer band for $[(bpy)_2(CO)Os^{II}(4,4'-bpy)Os^{III}(phen)(dppe)(Cl)]^{4+}$ in CH₃CN, (4) emission spectra of the bpa complexes at 25 °C in CH₂Cl₂, and (5) emission decay and triple exponential fit of the data for $[(bpy)_2(CO)Os(bpa)Os(phen)(dppe)(Cl)]^{3+}$ (5 pages). Ordering information is available on any current masthead page.