surroundings of manganese(II) coordinated by six bulky solvent molecules such as acetic acid or DMF should be sterically crowded. Therefore, the distance between manganese(II) and two donor atoms of the two equivalent bulky entering and leaving solvent molecules participating in the activation state would have to be longer than in nonbulky solvents such as water, methanol, and acetonitrile. The effect of the bulkiness of solvent and/or ligand on the activation volume observed in the complexation of iron(III) as mentioned in the Introduction is still valid for the solvent exchange of manganese(II).

Manganese(II) acetate is the solvolyzed species of manganese(II) perchlorate in acetic acid. As apparent from Table II, the activation volume for acetic acid exchange of manganese(II) acetate is definitely larger and the exchange rate of manganese(II) acetate is about 3 times faster than that of manganese(II) perchlorate. The enhanced rate of the solvent exchange or the ligand substitution on solvolyzed species has been observed also in other systems. Some complex formations in water are faster for the hydroxopentaaquairon(III) ion than for the hexaaquairon(III) ion.[6,7] The activation volume is negative for $Fe(H_2O)_6^{3+}$, while it is positive for $Fe(H_2O)_5(OH)^{2+}$.[6,7] Moreover, the kinetics of water exchange have been investigated for trivalent metal ions such as Ga^{3+}, Fe^{3+}, Cr^{3+}, and Ru^{3+} and for their monohydroxo species.[4,24,25] Water-exchange rates for monohydroxo species are some orders of magnitude faster than for hexaaqua species. The activation volumes for monohydroxo species are larger than those for corresponding hexaaqua species.

It is considered that the coordinated solvent molecules are labilized by the electron donation from the bound ligands such as CH_3COO^- and OH^- to the metal ion in solvolyzed species and that the activation mode of the reaction is less associative. The labilization by the bound ligand has been discussed quantitatively on the basis of the electron-donating ability of the bound ligand and the softness parameter of the metal ion.[26] The measurement of activation volume led us to the general mechanistic aspect of labilization of solvent molecules by the bound ligand; i.e., the stretch of the bond between the metal ion and the leaving solvent molecule in the activation process becomes longer by the electron donation from the bound ligand and the electron donation will electrostatically disfavor the approach of the donor atom of an entering solvent molecule, and thus the electron donation will inhibit associative character.

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Registry No. $Mn(ClO_4)_2$, 13770-16-6; $Mn(OAc)_2$, 638-38-0; HOAc, 64-19-7.

Supplementary Material Available: Pressure dependence of $\pi(\Delta\nu_{solv})$ and k_{ex} for water exchange of the nickel(II) ion (Figure S1) (1 page). Ordering information is given on any current masthead page.

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Influence of Variations in the Chromophoric Ligand on the Properties of Metal-to-Ligand Charge-Transfer Excited States

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The effects of variations in the chromophoric ligand on the properties of the metal-to-ligand charge-transfer (MLCT) excited states in the series $[Os(PP)_3]^{2+}$, $[(PP)_2Os(py)_2]^{2+}$, and $[(PP)_2Os(LL)]^{2+}$ (PP = 2,2′-bipyridine, 1,10-phenanthroline, or a substituted derivative; py = pyridine; LL = das, dppm, dppb, dppene) have been investigated. From a series of electrochemical and photophysical measurements it has been determined that (1) substituent variations in the chromophoric ligands have a relatively minor effect on the $d\pi(Os)$ levels as evidenced by variations in $E_{1/2}$ values for the ground-state Os(III/II) couples, (2) linear correlations exist between metal-to-ligand charge-transfer (MLCT) absorption or emission band energies and the difference in metal-based oxidation and ligand-based reduction potentials, $E_{1/2}(Os^{III/II}) - E_{1/2}(PP^{0/-})$, and (3) a linear relationship between $\ln k_{nr}$ and the emission energy, E_{em}, exists, consistent with the "energy gap law". It appears that for nonradiative decay both the pattern of acceptor vibrations and the vibrationally induced electronic coupling term remain relatively constant as the chromophoric ligand is varied.

Introduction

Several recent studies based on polypyridyl complexes of Os(II) and Ru(II) have been aimed at developing a detailed understanding of the factors at the microscopic level that determine the properties of metal-to-ligand charge-transfer (MLCT) excited states. These studies, which have been summarized in a recent review,[2] have addressed, for example, the effects on photophysical properties of variations in nonchromophoric ligands,[3-7] in the solvent,[8] in the counterion,[9] and in the chromophoric ligands.[10,11] The results have led to a detailed picture of how excited-state

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Chart I

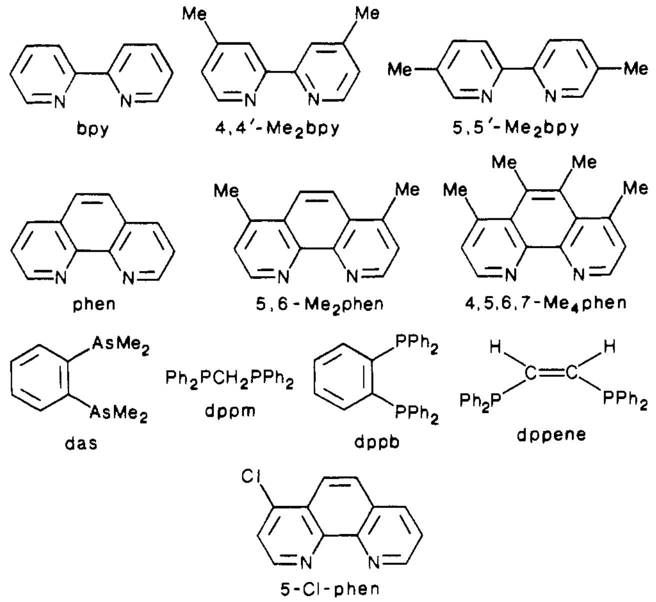

Table I. Electrochemical Data in CH_3CN–0.1 M $[NEt_4]ClO_4$ at 23 ± 2 °C vs the Saturated Sodium Chloride Electrode (SSCE)

no.	complex[a,b]	$E_{1/2}$-($Os^{III/II}$), V	$E_{1/2}$-($PP^{0/-}$), V	$\Delta E_{1/2}$, V[d]
1	$[Os(bpy)_3]^{2+}$	+0.81	−1.29	2.10
2	$[(bpy)_2Os(py)_2]^{2+}$	+0.75	−1.31	2.06
3	$[(bpy)_2Os(das)]^{2+}$	+1.11	−1.27	2.38
4	$[(bpy)_2Os(dppm)]^{2+}$	+1.27	−1.26	2.53
5	$[(bpy)_2Os(dppb)]^{2+}$	+1.34	−1.26	2.60
6	$[(bpy)_2Os(dppene)]^{2+}$	+1.34	−1.27	2.61
7	$[Os(4,4'\text{-}Me_2bpy)_3]^{2+}$	+0.66	−1.38	2.04
8	$[(4,4'\text{-}Me_2bpy)_2Os(PMe_2Ph)_2]^{2+}$	+0.90	−1.42	2.32
9	$[(4,4'\text{-}Me_2bpy)_2Os(das)]^{2+}$	+0.99	−1.39	2.38
10	$[(4,4'\text{-}Me_2bpy)_2Os(dppm)]^{2+}$	+1.20	−1.35	2.55
11	$[(4,4'\text{-}Me_2bpy)_2Os(dppb)]^{2+}$	+1.25	−1.38	2.63
12	$[(4,4'\text{-}Me_2bpy)_2Os(dppene)]^{2+}$	+1.26	−1.37	2.63
13	$[Os(phen)_3]^{2+}$	+0.82	−1.21	2.03
14	$[(phen)_2Os(py)_2]^{2+}$	+0.74	−1.30	2.04
15	$[(phen)_2Os(das)]^{2+}$	+1.11	−1.26	2.37
16	$[(phen)_2Os(dppb)]^{2+}$	+1.23	−1.24	2.47
17	$[(phen)_2Os(dppm)]^{2+}$	+1.32	−1.24	2.56
18	$[(phen)_2Os(dppene)]^{2+}$	+1.36	−1.23	2.59
19	$[(4,5,6,7\text{-}Me_4phen)_2Os(py)_2]^{2+}$	+0.62	−1.60	2.22
20	$[(4,5,6,7\text{-}Me_4phen)_2Os(PPh_3)(CN)]^{+}$	+0.76	−1.68[e]	2.44
21	$[(4,5,6,7\text{-}Me_4phen)_2Os(CH_3CN)_2]^{2+}$	+0.79	−1.63[e]	2.42
22	$[(4,5,6,7\text{-}Me_4phen)_2Os(dppm)]^{2+}$	+1.20	−1.45[e]	2.65
23	$[(4,5,6,7\text{-}Me_4phen)_2Os(dppene)]^{2+}$	+1.25	−1.51	2.76
24	$[(5,5'\text{-}Me_2bpy)_2Os(dppm)]^{2+}$	+1.24	−1.35[e]	2.59
25	$[(5\text{-}Cl\text{-}phen)_2Os(dppm)]^{2+}$	+1.24	−1.36	2.60
26	$[(5,6\text{-}Me_2phen)_2Os(dppm)]^{2+}$	+1.31	−1.29	2.60

[a] As PF_6^- salts. [b] See text for the ligand abbreviations. [c] $E_{1/2}$ for the first polypyridyl-based reduction. [d] $\Delta E_{1/2} = E_{1/2}(Os^{III/II}) - E_{1/2}(PP^{0/-})$. [e] Estimated; the wave is only quasi-reversible because of oxidation of the solvent or impurities in the solvent by Os(III). $E_{1/2}$ values were calculated from the peak potentials for the oxidative components.

properties are influenced by changes in electronic and molecular structure and by changes in the surrounding medium.

In our work in this area we have found the structurally related series of complexes $[(phen)Os(L)_4]^{2+}$ and $[(bpy)Os(L)_4]^{2+}$ (phen = 1,10-phenanthroline; bpy = 2,2′-bipyridine; L = $^1/_2$ bpy, pyr, CH_3CN, PR_3, etc.) to be of particular value.[2,5] By varying the nonchromophoric ligands while maintaining a constant basis for the chromophore, it has been possible to show that the most important factor dictating MLCT excited-state structure, radiative and nonradiative decay rates, absorption and emission energies, and redox potentials is the MLCT energy gap, which correlates well with a simple ground-state property, the metal-based Os(III/II) reduction potential.[5a] In this paper and two others,[13,14] we turn to the effect on MLCT excited-state properties of variations in the chromophoric ligand in complexes of Os(II). The structures and abbreviations for the chromophoric and nonchromophoric ligands used in the present study are illustrated in Chart I.

Experimental Section

Synthesis. $(PP)_2OsCl_2$ (PP = 4,4′-Dimethyl-2,2′-bipyridine (4,4′-Me_2bpy), 5-Chloro-1,10-phenanthroline (5-Cl-phen)). $[NH_4][OsCl_6]$ and 2 equiv of the ligand were heated at reflux in reagent grade ethylene glycol for 1–2 h. The cooled reaction mixture was treated with aqueous sodium dithionite to reduce any $[(PP)_2OsCl_2]^+$ that might have formed. The dark violet precipitate was collected and washed copiously with water, acetone, and diethyl ether. Yields were 75–85% for PP = 4,4′-Me_2bpy and 50–60% for PP = 5-Cl-phen. The products were used directly in subsequent reactions without further purification.

$[Os(PP)_3][PF_6]_2$ (PP = 4,4′-Me_2bpy, 5-Cl-phen). The salts were prepared by two different routes. The first involved heating *cis*-$[Os(PP)_2Cl_2]$ and 1.1 equiv of PP at reflux in a 1:1 ethanol:water mixture for 2 h under N_2. To the cooled reaction mixture was added saturated aqueous NH_4PF_6. The ethanol was removed with a rotary evaporator and the mixture was filtered, yielding a greenish solid. The product was purified by chromatography on basic alumina using a 1:1 acetonitrile:toluene mixture as the mobile phase. A green band accounting for most of the product was collected and the solvent was evaporated, giving $[Os(PP)_3][PF_6]_2$ in 30–45% yield. In the second method the intermediate $(PP)_2OsCl_2$ was not isolated. $[NH_4][OsCl_6]$ and 3.3 equiv of PP were heated at reflux in reagent grade ethylene glycol for approximately 1 h. The reaction mixture was worked up in a manner identical with that for the first method, giving yields of 80% for PP = 4,4′-Me_2bpy and 50–60% for PP = 5-Cl-phen. Elemental analysis for the previously unreported salt $[(4,4'\text{-}Me_2bpy)_3Os][PF_6]_2$ is as follows. Found (calcd): C, 41.36 (41.86); H, 4.24 (3.52); N, 7.89 (8.13).

$[(PP)_2Os(LL)][PF_6]_2$ (PP = 4,4′-Me_2bpy, 5,5′-Me_2bpy, 5-Cl-phen; LL = Bis(diphenylphosphino)methane (dppm), 1,2-Bis(dimethylarsino)benzene (das), Bis(dimethylphenylphosphine) $(PMe_2Ph)_2$, 1,2-Bis(diphenylphosphino)benzene (dppb), *cis*-1,2-Bis(diphenylphosphino)ethene (dppene)). $(PP)_2OsCl_2$ and a 5-fold excess of LL were heated at reflux under N_2 in ethylene glycol for 1–2 h (an 8-fold excess for LL = $(PMe_2Ph)_2$ and 3–5-h period of reflux). Upon addition of aqueous NH_4PF_6, an orange (green for LL = $(PMe_2Ph)_2$) precipitate formed and was collected. The solid was purified by chromatography as described above for the $(PP)_3$ complexes. The orange (green for LL = $(PMe_2Ph)_2$) band was collected, the solvent removed, and the product reprecipitated from acetone/ether to give yields that were generally on the order of 50%. Elemental analyses for salts which had not been previously reported are as follows. Found (calcd) for $[(4,4'\text{-}Me_2bpy)_2Os(dppm)][PF_6]_2$: C, 47.52 (47.73); H, 3.54 (3.77); N, 4.30 (4.54). Found (calcd) for $[(4,4'\text{-}Me_2bpy)_2Os(das)][PF_6]_2$: C, 35.68 (35.98); H, 3.65 (3.56); N, 4.80 (4.94). Found (calcd) for *cis*-$[(4,4'\text{-}Me_2bpy)_2Os(PMe_2Ph)_2][PF_6]_2$: C, 42.69 (42.70); H, 3.47 (4.13); N, 4.85 (4.98). Found (calcd) for $[(4,4'\text{-}Me_2bpy)_2Os(dppene)][PF_6]_2$: C, 47.07 (48.23); H, 3.46 (3.73); N,

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Table II. Spectroscopic Properties and Excited-State Parameters in CH_3CN at Room Temperature

no.	complex[a]	λ_{max}^{abs}, nm[b]	λ_{max}^{em}, nm[b]	τ, ns[c]	ϕ_{em}[d]	$10^{-5}k_r$, s^{-1} [e]	$10^{-6}k_{nr}$, s^{-1} [e]
1	$[Os(bpy)_3]^{2+}$	640	746	60	0.005	0.83	16.6
2	$[(bpy)_2Os(py)_2]^{2+}$	650[e]	769	41	0.004	0.98	24.3
3	$[(bpy)_2Os(das)]^{2+}$	518	682	151	0.019	1.3	6.50
4	$[(bpy)_2Os(dppm)]^{2+}$	475	644	304	0.056	1.8	3.11
5	$[(bpy)_2Os(dppb)]^{2+}$	470	636	344	0.049	1.4	2.76
6	$[(bpy)_2Os(dppene)]^{2+}$	466	630	500	0.070	1.4	1.86
7	$[Os(4,4'\text{-}Me_2bpy)_3]^{2+}$	600	780	36			27.8
8	$[(4,4'\text{-}Me_2bpy)_2Os(PMe_2Ph)_2]^{2+}$	600	691	134	0.021	1.6	7.31
9	$[(4,4'\text{-}Me_2bpy)_2Os(das)]^{2+}$	528	686	135	0.012	0.90	7.32
10	$[(4,4'\text{-}Me_2bpy)_2Os(dppm)]^{2+}$	488[f]	650	279	0.051	1.8	3.40
11	$[(4,4'\text{-}Me_2bpy)_2Os(dppb)]^{2+}$	483[f]	640	302	0.041	1.4	3.18
12	$[(4,4'\text{-}Me_2bpy)_2Os(dppene)]^{2+}$	464[f]	635	356	0.029	0.81	2.73
13	$[Os(phen)_3]^{2+}$	650	720	262	0.016	0.61	3.76
14	$[(phen)_2Os(py)_2]^{2+}$	670	746	143	0.008	1.0	1.55
15	$[(phen)_2Os(das)]^{2+}$	416	665	608	0.061	1.0	0.679
16	$[(phen)_2Os(dppb)]^{2+}$	476[f]	633	1281	0.14	1.3	0.751
17	$[(phen)_2Os(dppm)]^{2+}$	500	624	1130	0.15	1.3	0.414
18	$[(phen)_2Os(dppene)]^{2+}$	455	609	1840	0.24	1.3	0.414
19	$[(4,5,6,7\text{-}Me_4phen)_2Os(py)_2]^{2+}$	552	721	356	0.021	0.59	2.75
20	$[(4,5,6,7\text{-}Me_4phen)_2Os(PPh_3)(CN)]^{+}$	524[f]	692	1064	0.038	0.36	0.904
21	$[(4,5,6,7\text{-}Me_4phen)_2Os(CH_3CN)_2]^{2+}$	520[f]	668	1235	0.089	0.72	0.738
22	$[(4,5,6,7\text{-}Me_4phen)_2Os(dppm)]^{2+}$	458[f]	606	1826	0.29	1.59	0.389
23	$[(4,5,6,7\text{-}Me_4phen)_2Os(dppene)]^{2+}$	450	594	3462	0.21	0.61	0.228
24	$[(5,5'\text{-}bpy)_2Os(dppm)]^{2+}$	480[f]	620	714	0.054	0.76	1.32
25	$[(5'\text{-}Cl\text{-}phen)_2Os(dppm)]^{2+}$	508[f]	628	1060	0.067	0.63	0.880
26	$[(5,6\text{-}Me_2phen)_2Os(dppm)]^{2+}$	509[f]	625	1135	0.088	0.78	0.803

[a] As PF_6^- salts. See text for the ligand abbreviations. [b] ±2 nm. [c] Lifetime; ±2%. [d] Radiative efficiency; ±10%. [e] Calculated by using eq 1; ±10% for k_r; ±5% for k_{nr}. [f] Shoulder on a higher energy charge-transfer band.

4.25 (4.50). Found (calcd) for $[(5\text{-}Cl\text{-}phen)_2Os(dppm)][PF_6]_2$: C, 47.41 (45.48); H, 3.14 (2.81); N, 3.63 (4.33).

The other salts used in the study were prepared previously.[4a,5a,15]

Measurements. UV–visible absorption spectra were measured in acetonitrile with a Bausch and Lomb Model 210 spectrophotometer. Electrochemical measurements were made vs the saturated sodium calomel electrode (SSCE) in N_2-bubble-degassed acetonitrile. The supporting electrolyte was tetraethylammonium perchlorate at a concentration of ~0.1 M. The $E_{1/2}$ values for reversible couples were calculated as the average of the E_{peak} values for the anodic and cathodic waves from cyclic voltammetry. The electrochemical apparatus has been previously described.[16]

Emission spectra were measured with an SLM Instruments, Inc., Model 8000 photon-counting fluorometer. Spectra were corrected for detector response with programs and data supplied by the manufacturer. Emission quantum yields were determined in dry, N_2-purged acetonitrile solution at 23 ± 2 °C relative to $[(Ru(bpy)_3][PF_6]_2$ ($\phi_{em} = 0.062$).[8b] Luminescence lifetimes were obtained by laser flash photolysis using an apparatus that was described elsewhere.[17] Elemental analyses were performed by Integral Microlabs, Raleigh, NC.

Results

Electrochemistry. In Table I are listed half-wave potentials for the metal-centered Os(III/II) oxidation and the first (i.e., least negative) bpy- or phen-based reductions for the series of complexes. The data for the unsubstituted bpy and phen complexes have been reported previously[3,5] but are included along with their excited-state properties in Table II in order to provide a basis for comparison with the cases where there are substituted chromophoric ligands. From the data it is clear that, within a series in which the polypyridyl ligand remains unchanged, the ligand-based reduction potential is essentially constant. On the other hand, the metal-based Os(III/II) potential does vary considerably with the nature of the non-polypyridyl ligands. The trends that appear in the redox potentials are consistent with localization of the added electron in an orbital largely π^* in character on the chromophoric polypyridyl ligands in the reduced complexes and oxidation at levels largely $d\pi(Os)$ in character. Within a series, changes from pyridyl-type ligands to the more π-accepting phosphines cause an increase in $E_{1/2}(Os^{III/II})$, in large part by stabilization of the $d\pi$ levels due to enhanced back-bonding to the phosphines. Such effects are transmitted to the π^* levels of the chromophoric ligands, but through a secondary electronic interaction via $d\pi$–π^* mixing, and the ligand-based redox potentials remain very nearly constant. The effect of substituent changes at the chromophoric ligands of interest here have a relatively minor effect on the $d\pi(Os)$ levels, as shown by making an internal comparison of $E_{1/2}(Os^{III/II})$ values for the series $[(PP)_2Os(dppm)]^{2+}$, in which the nonchromophoric ligand is constant but the chromophoric ligand is varied.

Spectra. In Table II are listed absorption spectral maxima for the lowest energy MLCT visible absorption band that appears in the complexes arising from the transitions.

$$\underset{(d\pi)^6}{[(PP)Os^{II}(L)_4]^{2+}} \xrightarrow{h\nu} \underset{(d\pi)^5(\pi_1^*)}{[(PP^{\bullet-})Os^{III}(L)_4]^{2+*}}$$

The absorption spectra[18] are generally complex and consist of a series of MLCT transitions to the lowest lying π^* level of the ligand (π_1^*) and at higher energies to π_2^* with ligand-localized π–π^* transitions appearing in the UV.[18] Because of significant spin–orbit coupling, at the metal, the MLCT excited-state manifold includes MLCT transitions to states both largely singlet and largely triplet in character with the "triplet" components appearing on the low-energy side of the spectra with diminished intensities.[19] Emission occurs from lower energy, largely triplet states, which from the results of temperature-dependent lifetime studies behave kinetically as a single state by room temperature.[20] Complications may exist for some of the complexes by contributions to nonradiative decay from thermal population and decay of an additional low-lying, fourth MLCT state.[2,7a–c,21] Emission

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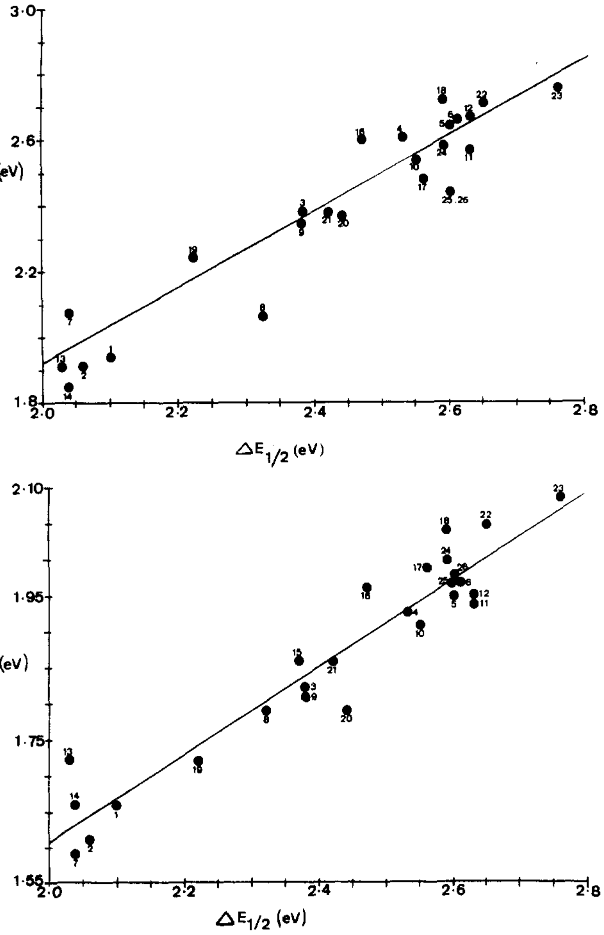

Figure 1. Top: E_{abs} (in CH_3CN) vs $\Delta E_{1/2}$ (=$E_{1/2}(Os^{III/II}$–$E_{1/2}(PP^{0/-})$ in 0.1 M $[NEt_4]ClO_4$–CH_3CN from the data in Tables I and II. The numbering code for the compounds is as in Table I. Bottom: E_{em} vs $\Delta E_{1/2}$ as in the top figure.

maxima, excited-state lifetimes, and emission quantum yields are also listed for the series of complexes in Table II.

As discussed earlier,[3,5,22] and given the electronic character of the MLCT excited states, it is expected that the energies of absorption

$$[(bpy)Os^{II}(bpy)_2]^{2+} \xrightarrow[E_{abs}]{} [(bpy^{\bullet-})Os^{III}(bpy)_2]^{2+*}$$

and emission

$$[(bpy^{\bullet-})Os^{III}(bpy)_2]^{2+*} \xrightarrow[E_{em}]{} [(bpy)Os^{II}(bpy)_2]^{2+}$$

will vary linearly with the difference in redox potentials for the metal-based Os(III/II) and ligand-based ($PP^{0/-}$) couples ($\Delta E_{1/2}$)

$$[Os(bpy)_3]^{3+} + [(bpy^{\bullet-})Os^{II}(bpy)_2]^{+} \xrightarrow[\Delta E_{1/2}]{} 2[Os(bpy)_3]^{2+}$$

where $\Delta E_{1/2} = E_{1/2}(Os^{III/II}) - E_{1/2}(PP^{0/-})$. That the predicted variation exists for both cases is shown in Figure 1. The linear correlations observed show that the same $d\pi$–π^* MLCT orbital origin is maintained for the series of polypyridyl ligands.

The slope of the plot of E_{abs} vs $\Delta E_{1/2}$ is 1.16 ± 0.14 and that of the plot of E_{em} vs $\Delta E_{1/2}$ is 0.61 ± 0.04. Slopes in excess of 1 for absorption and less than 1 for emission are expected.[5] The absorption and emission band energies include contributions from changes in equilibrium displacements between the excited and ground states for both intramolecular vibrations and solvent dipoles. Those changes *increase* and contribute to the band energies to a greater degree as the energy gap between the excited and ground states increases.

Excited-State Lifetimes. Rate constants for radiative (k_r) and nonradiative (k_{nr}) decay in Table II were determined from the measured lifetimes and emission quantum yields by using eq 1.

$$k_r = \phi_{em}/\tau \qquad (1a)$$

$$k_{nr} = 1/\tau - k_r \qquad (1b)$$

The calculations of k_r assume that the emitting excited states are formed with unit efficiency following excitation.

Discussion

Our goal in this work was to begin to investigate the effect on the nonradiative decay of MLCT excited states induced by changes in the chromophoric ligand. In earlier studies it was shown that systematic variations in MLCT excited-state properties exist for the two series $[(bpy)Os(L)_4]^{2+}$ and $[(phen)Os(L)_4]^{2+}$ (L = py, $^1/_2$ bpy, PR_3, CO, etc.).[3,5] The key to the systematic variations that exist lies in the effect of the ligands L on the energy gap between the excited and ground states (E_0). One finding was that the extent of bpy or phen distortion in the excited states increases with the energy gap. Another was that nonradiative decay rates follow the energy gap law both qualitatively and quantitatively.[2]

In the limit that nonradiative decay is dominated by a single mode or averaged mode M of quantum spacing $\hbar\omega_M$, for which $E_0 \gg \hbar\omega_M$ and $\hbar\omega_M \gg k_BT$, ln k_{nr} is given by[5b]

$$\ln k_{nr} = \ln \beta_0 - [\ln [\hbar\omega_M E_0/(1000\ \text{cm}^{-1})^2]]/2 - S_M + (\gamma + 1)^2(\Delta\bar{\nu}_{1/2}/\hbar\omega_M)^2/(16 \ln 2) - \gamma E_0/\hbar\omega_M \qquad (2a)$$

where

$$\beta_0 = C_k^2\omega_k(1\ \text{s})(\pi/2)^{1/2}/(1000\ \text{cm}^{-1}) \qquad (2b)$$

$$\gamma = \ln (E_0/S_M\hbar\omega_M) - 1 \qquad (2c)$$

In eq 2, C_k is the vibrationally induced electronic coupling integral between the initial and final states and ω_k is the angular frequency of the vibrational mode or modes responsible for the electronic coupling of the excited and ground states, the so-called "promoting" mode. S_M and ω_M are the Huang–Rhys factor and the angular frequency, respectively, of the principal accepting mode or, in this case, for an averaged ν(PP) ring-stretching mode, E_0 is the energy difference between the $v_M{}^* = 0$ and $v_M = 0$ vibrational levels for the two states, and $\Delta\bar{\nu}_{1/2}$ is the full width at half-maximum of the highest energy, resolved vibronic band in the emission spectrum and includes contributions from both low-frequency vibrations and the solvent.

In earlier work,[2,4,5b] it has been shown that, through a series of related complexes where E_0 is varied, γ remains relatively constant since the degree of excited-state distortion (S_M) increases with the energy separation between states (E_0). For such a case, eq 2a predicts that ln k_{nr} should decrease linearly as E_0 increases, at least in the limits of the validity of the approximations used to derive eq 2a. Microscopically, the origin of the linear decrease in ln k_{nr} as E_0 increases is in a lower overlap between the excited- and ground-state vibrational wave functions for the acceptor vibrations as the energy gap increases.

In an earlier study, where the focus was on variations in the nonchromophoric ligands, the various parameters required for the calculation of the Franck–Condon factors in eq 2—E_0, $\hbar\omega_M$, S_M, $\Delta\bar{\nu}_{1/2}$—were available from emission spectral fitting, which allowed for a quantitative evaluation of the validity of eq 2a.[5b] Emission spectral fitting results are not available for all the complexes reported here, but it is still possible to make a qualitative comparison based on eq 2 since, to a good approximation, E_0 is proportional to E_{em}.[4]

In Figure 2 are shown plots of ln k_{nr} vs E_{em} for the four series of chromophoric ligands. There are insufficient data for a precise comparison, but the trends are obvious. The plots show that ln k_{nr} does vary linearly with E_{em} as expected and that the individual members of the bpy-based and phen-based families lie on overlapping lines. The composite lines for the bpy- and phen-based cases are roughly parallel.

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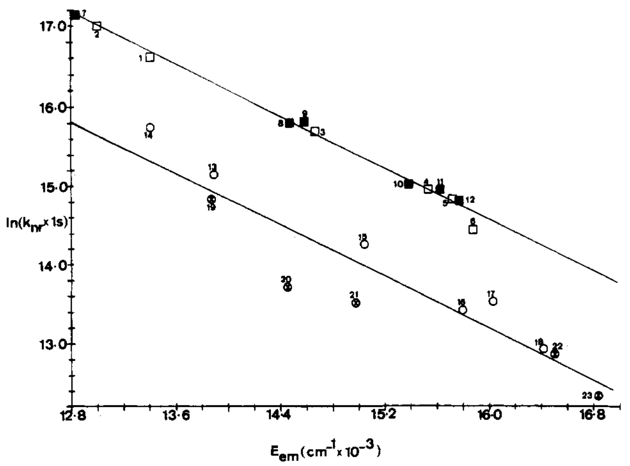

Figure 2. ln (k_{nr} × 1 s) vs E_{em} in CH_3CN at room temperature, based on the data in Table II with the numbering code as in Table I. Complexes are designated as follows: □, bpy; ■, 4,4-'Me_2bpy; ○, phen; ⊗, 4,5,6,7-Me_4phen. The numbering code is as in Table I.

The slopes and intercepts of the ln k_{nr} vs E_{em} plots in Figure 2 are (−0.82 ± 0.02) × 10^3 cm^{-1} and 27.6 ± 0.4, respectively, for the bpy-based cases and (−0.82 ± 0.1) × 10^3 cm^{-1} and 26.3 ± 1.6 for the phen-based cases. The values of the slopes and intercepts are consistent with those found earlier for polypyridyl-based MLCT excited states of Ru(II) and Os(II), where variations in E_0 were induced by changes in nonchromophoric ligands,[3-5] solvent,[8a,b] ion pairing,[9] or the glass to fluid transition in a 4:1 (v:v) EtOH/MeOH solution.[8c] Given the parameters that determine the correlation and the slopes of the lines (S_M, $\hbar\omega_M$, etc.), it appears that the pattern and frequencies of the dominant acceptor vibrational modes remain relatively constant through the two series. For MLCT excited states based on 2,2′-bipyridine, the results of resonance Raman experiments have shown that the principal accepting modes for the MLCT excited states are a series of seven or eight totally symmetric ν(bpy) ring-stretching modes.[7e,23] The substituent-induced mixing of other local modes into these ring-based normal modes in the substituted bpy and phen complexes may change the reduced masses of the vibrations, but apparently, the changes in substituents do not lead to gross changes in the nature or frequencies of the accepting modes at least for the rather limited range of ligands studied here. This is not a surprising result since, for a series of substituted pyridines, the frequencies of the ring-stretching modes are known to be relatively insensitive to substitutions of the ring H atoms by methyl or halide groups.[24]

Given the form of eq 2, the parallel but offset nature of the correlations for the bpy and phen complexes would appear to imply that the vibrationally induced electronic coupling term ln β_0 might be different for the two types of ligands. However, in the quantitative study alluded to earlier, the difference between bpy and phen was shown *not* to have its origin in an electronic effect.[5b] Rather, in a comparison of analogous bpy and phen complexes based on the results of emission spectral fitting, the bpy complexes were found to have systematically smaller values of E_0 and larger values of S_M. The differences in the response of the two ligands to the presence of the excited electron give rise, on the average, to an increase in k_{nr} by a factor of ~3 for bpy complexes compared to their phen analogues.[5b]

For the series of complexes studied here, the same conclusions are reached as shown graphically in Figures 3 and 4. In Figure 3 the data in Figure 2 have been replotted as ln k_{nr} vs E_{em} for the bpy complexes and as ln ($3k_{nr}$) vs E_{em} for the phen complexes.

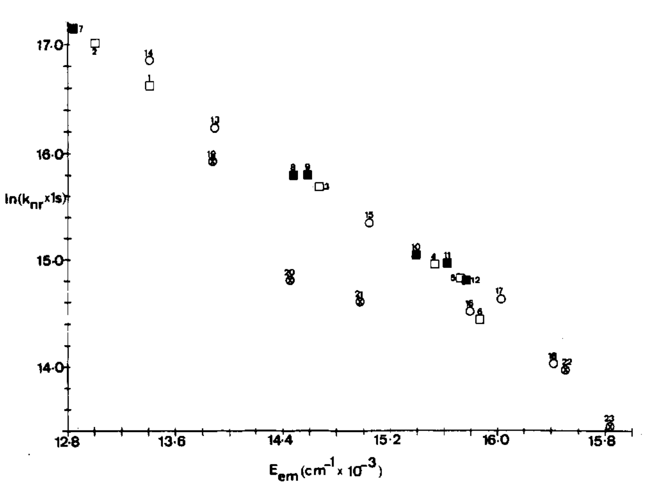

Figure 3. Plots of ln (k_{nr} × 1 s) vs E_{em} for the bpy-based MLCT excited states and ln ($3k_{nr}$ × 1 s) vs E_{em} for the phen-based excited states in CH_3CN at room temperature. The numbering code is as in Table I. Complexes are designated as follows: □, bpy; ■, 4,4′-Me_2bpy; ○, phen; ⊗, 4,5,6,7-Me_4phen.

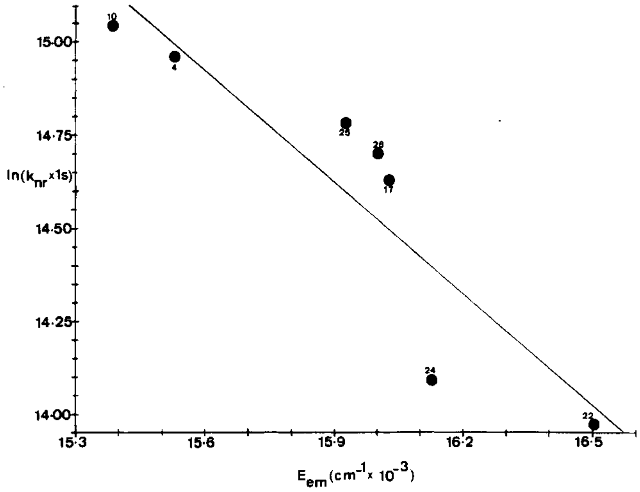

Figure 4. Plot of ln (k_{nr} × 1 s) or ln ($3k_{nr}$ × 1 s) vs E_{em} for the phen derivatives in the series $[(PP)_2Os(dppm)]^{2+}$ in CH_3CN at room temperature. The numbering code is as in Table I.

When the average factor of 3 is included for the phen-based MLCT states, all of the complexes follow the same correlation regardless of whether the basis for the chromophoric ligand is 2,2′-bipyridine or 1,10-phenanthroline, at least for the limited set of excited states available. The point is further illustrated in Figure 4, where values of ln k_{nr} for bpy-based MLCT states or ln ($3k_{nr}$) for the phen-based MLCT states are plotted vs E_{em} for the series of complexes $[(PP)_2Os(dppm)]^{2+}$, in which the dppm ligand is held constant while the chromophoric ligand is varied. A linear correlation is again observed with slope (−1.0 ± 0.2) × 10^3 cm^{-1} and intercept 31 ± 3.

The linearity of plots of this kind and the coincidence of slopes and intercepts suggest that, once the systematic difference in E_0 and S_M between equivalent bpy and phen complexes is taken into account, the pattern of acceptor vibrations remains relatively constant. It also suggests that the electronic coupling term, β_0 in eq 2b, must remain relatively constant, at least through the somewhat limited series for which data are presented here.

The vibrationally induced electronic coupling integral for nonradiative decay is given by

$$C_k = \hbar\left\langle \psi_i \left| \frac{\partial}{\partial Q_k} \right| \psi_f \right\rangle$$

where ψ_i and ψ_f are the electronic wave functions for the initial and final states and Q_k is the mass-weighted normal coordinate for the "promoting" mode(s).[25] Given the electronic character

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of the excited ($(d\pi)^5(\pi_1^*)^1$) and ground states ($(d\pi)^6$), C_k is of the form

$$C_k = \hbar\left\langle \pi_1^* \middle| \frac{\partial}{\partial Q_k} \middle| d\pi_3 \right\rangle$$

where π_1^* is the lowest π^* level of the acceptor ligand and $d\pi_3$ is the largely metal-based $d\pi$ orbital that contains the electron "hole" in the excited state. On the basis of the LCAO approximation, π_1^* can be written as the sum $\pi_1^* = a_N 2p_N + a_{C_1} 2p_{C_1} + ...$, where a_N, a_{C_1}, ... are the expansion coefficients and $2p_N$, $2p_{C_1}$ are the p–π orbital contributors to π_1^* by the atoms of the ring. The metal ion is directly bound to the N atom of the ring so that significant, direct orbital overlap is only expected to exist between $d\pi$ and $2p_N$ and not between $d\pi$ and $2p_C$ for the relatively distant C atoms. If $d\pi$–$2p_C$ overlap is neglected, C_k is given by

$$C_k \sim a_N \hbar \left\langle 2p_N \middle| \frac{\partial}{\partial Q_k} \middle| d\pi_3 \right\rangle \tag{3}$$

Given the form of eq 3, it may not be too surprising that significant variations in β_0 do not appear with variations in chromophoric ligands studied here. For these ligands CNDO/2 molecular orbital calculations[26] show that relatively small variations occur in the $2p_N$, $2p_C$ atomic compositions of π_1^* and, in particular, that variations in a_N are small. For significant electronic substituent effects to appear, it may be necessary to turn to more dramatic variations in the electronic character of the substituents on the chromophoric ligands.

Conclusions. From our results, variations in the chromophoric ligand in polypyridyl complexes of Os(II) lead to systematic variations in the ligand-based π^* (acceptor) and metal-based $d\pi$ (donor) levels as shown by electrochemical measurements. These variations, in turn, dictate variations in absorption and emission band maxima and the magnitude of the energy gap between the excited and ground states. At room temperatue, excited-state lifetimes for the series of excited states studied are determined largely by nonradiative decay, where the major role as energy acceptor is played by a series of medium-frequency ν(bpy) or ν(phen) ring-stretching modes. The pattern of acceptor modes appears to remain constant as the chromophoric ligand is varied with a systematic difference existing between bpy and phen as chromophoric ligands, arising from a subtly different structural response to the excited electron. At least in the limited series studied here, the dynamic, vibrationally induced electronic coupling term remains relatively constant throughout the series.

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Registry No. $[Os(bpy)_3][PF_6]_2$, 75441-79-1; $[(bpy)_2Os(py)_2][PF_6]_2$, 115304-13-7; $[(bpy)_2Os(das)][PF_6]_2$, 80502-60-9; $[(bpy)_2Os(dppm)][PF_6]_2$, 75441-73-5; $[(bpy)_2Os(dppb)][PF_6]_2$, 80502-64-3; $[(bpy)_2Os(dppene)][PF_6]_2$, 75441-75-7; $[Os(4,4'\text{-}Me_2bpy)_3][PF_6]_2$, 99328-31-1; $[(4,4'\text{-}Me_2bpy)_2Os(PMe_2Ph)_2][PF_6]_2$, 115245-82-4; $[(4,4'\text{-}Me_2bpy)_2Os(das)][PF_6]_2$, 115245-84-6; $[(4,4'\text{-}Me_2bpy)_2Os(dppm)][PF_6]_2$, 115245-86-8; $[(4,4'\text{-}Me_2bpy)_2Os(dppb)][PF_6]_2$, 115245-88-0; $[(4,4'\text{-}Me_2bpy)_2Os(dppene)][PF_6]_2$, 115245-90-4; $[Os(phen)_3][PF_6]_2$, 75441-76-8; $[(phen)_2Os(py)_2][PF_6]_2$, 115304-15-9; $[(phen)_2Os(das)][PF_6]_2$, 80502-80-3; $[(phen)_2Os(dppb)][PF_6]_2$, 115245-91-5; $[(phen)_2Os(dppm)][PF_6]_2$, 75446-25-2; $[(phen)_2Os(dppene)][PF_6]_2$, 75446-27-4; $[(4,5,6,7\text{-}Me_4phen)_2Os(py)_2][PF_6]_2$, 115245-93-7; $[(4,5,6,7\text{-}Me_4phen)_2Os(PPh_3)(CN)][PF_6]$, 115245-95-9; $[(4,5,6,7\text{-}Me_4phen)_2Os(CH_3CN)_2][PF_6]_2$, 115245-97-1; $[(4,5,6,7\text{-}Me_4phen)_2Os(dppm)][PF_6]_2$, 115245-99-3; $[(4,5,6,7\text{-}Me_4phen)_2Os(dppene)][PF_6]_2$, 115246-01-0; $[(5,5'\text{-}Me_2bpy)_2Os(dppm)][PF_6]_2$, 115246-03-2; $[(5\text{-}Cl\text{-}phen)_2Os(dppm)][PF_6]_2$, 115246-05-4; $[(5,6\text{-}Me_2phen)_2Os(dppm)][PF_6]_2$, 115246-07-6; $(4,4'\text{-}Me_2bpy)_2OsCl_2$, 115304-16-0; $(5\text{-}Cl\text{-}phen)_2OsCl_2$, 115246-08-7; $[Os(5\text{-}Cl\text{-}phen)_3][PF_6]_2$, 115246-10-1; $[Os(bpy)_3][PF_6]_3$, 28277-56-7; $[(bpy)_2Os(py)_2][PF_6]_3$, 115304-18-2; $[(bpy)_2Os(das)][PF_6]_3$, 115246-12-3; $[(bpy)_2Os(dppm)][PF_6]_3$, 115246-14-5; $[(bpy)_2Os(dppb)][PF_6]_3$, 115246-16-7; $[(bpy)_2Os(dppene)][PF_6]_3$, 115246-18-9; $[Os(4,4'\text{-}Me_2bpy)_3][PF_6]_3$, 28392-64-5; $[(4,4'\text{-}Me_2bpy)_2Os(PMe_2Ph)_2][PF_6]_3$, 115246-20-3; $[(4,4'\text{-}Me_2bpy)_2Os(das)][PF_6]_3$, 115246-22-5; $[(4,4'\text{-}Me_2bpy)_2Os(dppm)][PF_6]_3$, 115246-24-7; $[(4,4'\text{-}Me_2bpy)_2Os(dppb)][PF_6]_3$, 115246-26-9; $[(4,4'\text{-}Me_2bpy)_2Os(dppene)][PF_6]_3$, 115246-28-1; $[Os(phen)_3][PF_6]_3$, 36491-38-0; $[(phen)_2Os(py)_2][PF_6]_3$, 115304-20-6; $[(phen)_2Os(das)][PF_6]_3$, 115246-30-5; $[(phen)_2Os(dppb)][PF_6]_3$, 115246-32-7; $[(phen)_2Os(dppm)][PF_6]_3$, 115246-34-9; $[(phen)_2Os(dppene)][PF_6]_3$, 115246-36-1; $[(4,5,6,7\text{-}Me_4phen)_2Os(py)_2][PF_6]_3$, 115246-38-3; $[(4,5,6,7\text{-}Me_4phen)_2Os(CH_3CN)_2][PF_6]_3$, 115246-40-7; $[(4,5,6,7\text{-}Me_4phen)_2Os(dppm)][PF_6]_3$, 115246-42-9; $[(4,5,6,7\text{-}Me_4phen)_2Os(dppene)][PF_6]_3$, 115246-44-1; $[(5,5'\text{-}Me_2bpy)_2Os(dppm)][PF_6]_3$, 115246-46-3; $[(5\text{-}Cl\text{-}phen)_2Os(dppm)][PF_6]_3$, 115246-48-5; $[(5,6\text{-}Me_2phen)_2Os(dppm)][PF_6]_3$, 115246-50-9; $[NH_4][OsCl_6]$, 115246-51-0; $[(4,5,6,7\text{-}Me_4Phen)_2Os(PPh_3)(CN)][PF_6]_2$, 115419-69-7.

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