# The Influence of Environmental Effects on Excited-State Lifetimes. The Effect of Ion Pairing on Metal-to-Ligand Charge Transfer Excited States

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Excited-state emission and lifetimes are reported for the complexes  $Os(phen)_3^{2+}$  and  $Os(4,4'-Ph_2phen)_3^{2+}$  (phen is 1,10phenanthroline; 4,4'-Ph2phen is 4,4'-diphenyl-1,10-phenanthroline) as a function of counterion in CH2Cl2 solution. The changes in nonradiative decay rate constants are observed to vary with changes in emission energy maxima as predicted by the energy gap law. The variations in emission energies and through them the decay rates appear to be induced by changes in ion-dipole interactions in the excited state.

#### Introduction

The results of a series of studies on metal-to-ligand charge transfer (MLCT) excited states based on  $(d\pi)^6$ -polypyridine-metal complexes have led to detailed insight into the molecular features that determine the photophysical properties of the excited states.<sup>1-17</sup> This is especially true for complexes of Ru(II) and Os(II) where the results of low-temperature emission, temperature-dependent lifetime, resonance Raman, and radiative efficiency measurements have revealed, among other things, the pattern of intramolecular vibrations which determine emission band shapes and which in turn act as acceptor vibrations for nonradiative excited-state decay.

Rate constants for excited-state radiative decay,  $k_r$ , are predicted to vary with the cube of the emission energy,  $E_{\rm em}$ , and with the transition moment integral  $\mu = \langle \psi_{gs} | \hat{\mu} | \psi_{es} \rangle$  as  $(E_{em} \text{ in ergs.})^{18}$ 

$$k_{\rm r} = \frac{4E_{\rm em}^3}{3\hbar^4} |\langle \psi_{\rm gs} | \hat{\mu} | \psi_{\rm es} \rangle|^2 \tag{1}$$

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 $\psi_{gs}$  and  $\psi_{es}$  are the excited- and ground-state electronic wave functions and  $\hat{\mu}$  is the transition dipole moment operator. Rate constants for nonradiative decay<sup>19,20</sup>

$$k_{\rm nr} = C_{\rm k}^{2} \omega_{\rm k} \sum_{v'} \sum_{v''} \prod_{j} P_{v'} \langle x_{v'} | x_{v''} \rangle^{2}$$

$$C_{\rm k}^{2} = \frac{\hbar^{2}}{M_{\rm k}} |\langle \psi_{\rm gs} | i\partial / \partial Q_{\rm k} | \psi_{\rm es} \rangle^{2} |$$
(2)

are determined by the product of two factors. The first is the vibrationally induced mixing between the electronic ground and excited states,  $C_k^2 \omega_k$ , induced by the "promoting" vibration of angular frequency  $\omega_k$  (=  $2\pi \nu_k$ ), displacement coordinate  $Q_k$ , and reduced mass  $M_k$ . In eq 2 it is assumed that vibrationally induced mixing of the states is dominated by a single promoting vibration. The second term in eq 2 is the vibrational overlap or Franck-Condon term. In it are included possible contributions from all of the normal vibrations of the system including the surrounding medium. The product in eq 2 is over all the normal vibrations, j. The sums of vibrational wave functions,  $\chi$ , are for a given normal mode j and are over all of the vibrational levels of the excited state,  $\chi_v$ , and of the ground state,  $\chi_{v''}$ . v' and v'' are the vibrational quantum numbers of the excited- and ground-state vibrational levels. The  $P_{v'}$  are population factors for the excited-state levels,  $\chi_{\nu'}$ . In practice, the only nonunity contributions in the vibrational overlap term arise from those normal vibrations for which there is either a change in equilibrium displacement between the two electronic states or for which there is a change in vibrational frequency. If the usually relatively small contributions from frequency changes are neglected, the linear approximation, and it is assumed that the harmonic oscillator approximation is valid, the individual vibrational overlap integrals which appear in eq 2 are given by eq 3 for the v' = 0 level of the

$$|\langle \chi_{v'=0} | \chi_{v''} \rangle|^2 = (S^{v''} / v!) \exp(-S)$$
(3)

state. In eq 3, S is related to the difference in the dimensionless fractional displacement coordinate between the ground and excited states,  $\Delta$ , by  $S = 1/2\Delta^2$ . In turn,  $\Delta$  is related to the difference in the equilibrium displacement coordinates for the normal mode between the ground and excited states,  $\Delta Q_{\rm e}$ , by  $\Delta = \Delta Q_{\rm e} (M\omega/M)$ h)<sup>1/2</sup>. Equation 2 has been solved for a number of limiting conditions including the low temperature, weak vibrational coupling limit. In this limit the extent of excited-state distortion is relatively small, S < 1, and since  $\hbar \omega >> k_{\rm B}T$  population of vibrational levels above v' = 0 can be neglected. Assuming the low temperature, weak vibrational coupling limit for a high-frequency "acceptor" vibration having reduced mass  $M_{\rm M}$ , and angular frequency  $\omega_{\rm M}$ ,

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and a lower frequency acceptor vibration of reduced mass,  $M_L$ , and angular frequency,  $\omega_L$ , leads to eq 4.<sup>19-21</sup> The term in which

$$\ln k_{\rm nr} = (\ln \beta_0 - S_{\rm M}) - \frac{\gamma_0 E_{\rm em}}{\hbar \omega_{\rm M}} + \frac{\chi_0}{\hbar \omega_{\rm M}} \left[ \frac{k_{\rm B} T}{\hbar \omega_{\rm M}} (\gamma_0 + 1)^2 \right] + S_{\rm L} \left( \frac{\omega_{\rm L}}{\omega_{\rm M}} \right) (\gamma_0 + 1) \quad (4)$$
$$\beta_0 = C^2 \omega_{\rm k} \left[ \frac{\pi}{2\hbar \omega_{\rm M} E_{\rm em}} \right]^{1/2}$$
$$\gamma_0 = \ln \left( \frac{E_{\rm em}}{S_{\rm M} \hbar \omega_{\rm M}} \right) - 1$$

 $\omega_1$  appears is an approximation. In eq 4, contributions to excited-state decay from the collective vibrations of the surrounding medium are included in the high temperature, classical limit for which  $\hbar \omega_0 \ll k_{\rm B}T$ . The term  $\chi_0$  is four times the classical solvent vibrational trapping energy for the electron transfer act associated with the excited-state to ground-state transition.

When used in conjunction with photophysical measurements on a series of polypyridyl complexes of Os(II) of the type (NN)OsL<sub>4</sub><sup>2+</sup> (NN is 1,10-phenanthroline (phen) or 2,2'-bipyridine (bpy); L is PR<sub>3</sub>, AsR<sub>3</sub>, py, CH<sub>3</sub>CN,...) and related complexes of Ru(II), eq 4 has provided an adequate theoretical basis for describing in a quantitative way the nonradiative decay characteristics of the metal-to-ligand charge transfer (MLCT) excited states,  $(NN^{-})Os^{III}L_4^{2+*} \rightarrow (NN)Os^{II}L_4^{2+}$ .

Although the Os(II) complexes have somewhat complex electronic structures, 6,7,10-12 they have proven to be highly useful probes experimentally. The emission properties from the MLCT states appear to have a common electronic origin. Excited-state decay is dominated by medium-frequency acceptor vibrations largely ring stretching (polypyridine) in character with lesser contributions from low-frequency modes largely Os-L in character.

The osmium and related Ru complexes have proven to be of value in exploring the role of medium effects on excited-state photophysical properties.<sup>4b,23b</sup> For example, a suggestion has been made that the appearance of a significant  $H_2O-D_2O$  effect on MLCT excited-state nonradiative decay of  $Ru(bpy)_3^{2+*}$  could be attributed to significant mixing of charge transfer to solvent excited states into the nominally MLCT excited state.<sup>24</sup> However, recent work based on excited-state decay of a series of complexes of Os(II) in a variety of solvents has led to the suggestion that solvent effects can be reconciled on the basis of the energy gap law result in eq 4.4b,21,23b In non-hydroxylic solvents like acetonitrile or dichloromethane the effects of variations in solvent on  $k_{nr}$  are dictated by variations in the emission energy as predicted by equation 4 assuming that variations in  $\chi_0$  are relatively small. However, in hydroxylic solvents like water or methanol the solvent appears to become involved in excited-state decay in an additional way through collective modes which have significant O-H character.

With the availability of the theoretical results in eq 4 and the series of well-defined MLCT excited states based on Os(II), it became possible to explore medium effects in a systematic way. In this manuscript we explore the role of medium effects in further detail, in this case the origins of which lie in specific ion pairing by a series of different anions in the low-polarity solvent dichloromethane. It should be noted that such studies are difficult to carry out based on analogous complexes of Ru because of the intervention of low-lying dd states which contribute to nonradiative decay and to photodecomposition.<sup>2,3,4a-e</sup>

## **Experimental Section**

Preparations. The salt [Os(phen)<sub>3</sub>]Cl<sub>2</sub> was prepared by the reaction between (NH<sub>4</sub>)<sub>2</sub>[OsCl<sub>6</sub>] (0.133 g) and an excess of 1,10-phenanthroline (0.25 g) in 20 mL of ethylene glycol heated at reflux for 90 min as reported earlier.<sup>25</sup> The PF<sub>6</sub>, BPh<sub>4</sub>, and ClO<sub>4</sub> salts were prepared by metathesis by dissolving the Cl<sup>-</sup> salt in water and adding concentrated aqueous solutions of  $NH_4PF_6$ , NaBPh<sub>4</sub>, or  $[N(n-Bu)_4](ClO_4)$ , respectively. The salts, which precipitated immediately, were washed with cold water followed by diethyl ether and air dried. The halide salts,  $[Os(phen)_3]Cl_2$ and [Os(phen)<sub>3</sub>]Br<sub>2</sub>, were isolated as solids by metathesis reactions by the addition of concentrated solutions of  $[N(n-Bu)_4]Cl$  or  $[N(n-Bu)_4]Br$  in acetone to acetone solutions containing [Os- $(phen)_3](PF_6)_2$ . The halide salts which precipitated were washed several times with ether and air dried. We were unable to prepare pure samples of the corresponding thiocyanate or azide salts by this procedure. The thiocyanate salt,  $[Os(phen)_3](NCS)_2$ , was prepared by ion exchange of an acetone solution containing  $[Os(phen)_3](PF_6)_2$  using a Dowex 2-X8 anion exchange resin in the NCS<sup>-</sup> form. The salt was isolated as a brown solid by reducing the solution volume and precipitating by addition to stirring ether. The ion-exchange-isolation procedure was repeated until there was no evidence in the infrared (KBr pellets of the salt) for the  $PF_6^-$  anion ( $\nu(PF_6^-) = 745 \text{ cm}^{-1}$ ).

The  $Os(4,4'-Ph_2Phen)_3^{2+}$  salts were prepared in a manner analogous to the  $Os(phen)_3^{2+}$  salts.  $(NH_4)_2OsCl_6$  (0.08 g, 0.45 mM) and 4,4'-diphenyl-1,10-phenanthroline (4,4'-Ph<sub>2</sub>phen) (0.39 g) were heated in 20 mL of ethylene glycol at reflux for 2 h. In each case the isolation procedure paralleled that of the analogous  $Os(phen)_3^{2+}$  salts with the exception of the thiocyanate complex, which was isolated by metathesis of the  $PF_6^-$  salt in acetone.

Once isolated, all of the salts were purified by column chromatography on alumina (Fisher). Acetonitrile-methanol solvent mixtures were used for elution of the halide salts. All other salts were eluted with acetonitrile-toluene mixtures. The salts were isolated by evaporating the eluents to a small volume and precipitating the solids by addition to ether. The salts were reprecipitated from acetonitrile by addition to ether. The solids were collected by filtration and dried in vacuo. Infrared spectra of the salts as KBr pellets showed the absence of  $PF_6^-$  ( $\nu(PF_6^-) = 745$  $cm^{-1}$ ) and for the ClO<sub>4</sub>, BPh<sub>4</sub>, and NCS salts, the presence of characteristic IR bands for the anions at, for example,  $\nu(ClO_4^{-})$ = 625 cm<sup>-1</sup>,  $\nu(BPh_4^-) = 1475$  cm<sup>-1</sup>, and  $\nu(NCS^-) = 2053$  cm<sup>-1</sup>.

Lifetimes. Lifetimes were determined by observing transient emission decay at the emission maximum following pulsed excitation (pulse width  $\sim 10$  ns) by a Molectron Corporation nitrogen laser (Model UV-400) as described previously.4b The excited-state decays followed first-order kinetics. Lifetimes were calculated by averaging 60 intensity vs. time curves and plotting  $\ln (I)$  vs. time for an appropriate section of the average trace. Errors shown in Figure 2 and Table I reflect the statistical uncertainty found in these plots. Excited-state lifetimes  $(\tau)$  are related to the radiative  $(k_r)$  and nonradiative  $(k_{nr})$  rate constants for excited-state decay by  $1/\tau = k_r + k_{nr}$ . For the salts [Os- $(phen)_3](PF_6)_2$  and  $[Os(4,4'-Ph_2phen)_3](PF_6)_2$ , radiative efficiencies,  $\phi_e$ , are low; in acetonitrile at room temperature,  $\phi_e =$ 0.016 and 0.021, respectively. As a consequence, it follows from  $\phi_e = k_r \tau$  that  $k_r \ll k_{nr}$  and the lifetime measurements give  $k_{nr}$ directly via  $1/\tau = k_{nr}$ , with an acceptable degree of accuracy.

#### Results

Emission spectra for the series of salts containing  $Os(phen)_3^{2+}$ or  $Os(4,4'-Ph_2Phen)_3^{2+}$  were obtained at room temperature in CH<sub>2</sub>Cl<sub>2</sub> solution. All of the spectra were characterized by a single

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TABLE I: Emission and Lifetime Data (in CH<sub>2</sub>Cl<sub>2</sub> at Room Temperature)

salt	$E_{\rm em}$ , anm	$E_{\rm em},^{a} {\rm cm}^{-1} \times 10^{-3}$	$\tau$ , <sup>b</sup> ns	$10^{-6}k_{\rm nr}^{\ b}$	$\ln (k_{\rm nr})^b$	$fwhm, c cm^{-1} \times 10^{-3}$
$[Os(phen)_3](PF_6)_2$	700	14.29	315 ± 3	$3.17 \pm 0.03$	14.97	2.01
$[Os(phen)_3](ClO_4)_2$	705	14.18	297 ± 2	$3.36 \pm 0.02$	15.03	1.91
[Os(phen) <sub>3</sub> ]Cl <sub>2</sub>	714	14.01	$245 \pm 2$	$4.08 \pm 0.02$	15.22	2.02
$[Os(phen)_3]Br_2$	714	14.01	$260 \pm 2$	$3.84 \pm 0.02$	15.16	2.02
$[Os(phen)_3](SCN)_2$	708	14.12	$289 \pm 2$	$3.46 \pm 0.02$	15.06	2.14
$[Os(phen)_3](BPh_4)_2$	696	14.37	$357 \pm 2$	$2.80 \pm 0.02$	14.85	2.02
$[Os(4,4'-Ph_2phen)_3](PF_6)_2$	734	13.62	$312 \pm 2$	$3.20 \pm 0.02$	14.98	1.77
$[Os(4,4'-Ph_2phen)_3](ClO_4)_2$	741	13.50	$273 \pm 1$	$3.67 \pm 0.01$	1k.12	1.74
$[Os(4,4'-Ph_2phen)_3]Cl_2$	744	13.44	$262 \pm 2$	$3.82 \pm 0.02$	15.16	1.74
$[Os(4,4'-Ph_2phen)_3]Br_2$	741	13.50	$262 \pm 2$	$3.82 \pm 0.02$	15.16	1.74
$[Os(4,4'-Ph_2phen)_3](SCN)_2$	739	13.53	289 ± 1	$3.46 \pm 0.01$	15.06	1.83

<sup>a</sup> Emission maxima accurate to  $\pm 1$  nm or  $\pm 20$  cm<sup>-1</sup>. <sup>b</sup> The error limits reflect the statistical uncertainty obtained from first-order fits of 64 emission decay curves. Figure 2 reflects the estimated reproducibility of the data between separate sets of experiments ( $\pm 5\%$ ). <sup>c</sup> Full width at half-maximum of the emission band,  $\pm 40$  cm<sup>-1</sup>.



Figure 1. Emission spectra of  $[Os(phen)_3](BPh_4)_2$  (---) and  $[Os(phen)_3]Cl_2(---)$  in  $CH_2Cl_2$  solution at room temperature. The spectra have been corrected for variations in detector sensitivity with wavelength.

broad, asymmetric band with no well-defined structure. Spectra of the salts  $[Os(phen)_3]Cl_2$  and  $[Os(phen)_3](BPh_4)_2$  are shown in Figure 1. It should be noted that for these and related complexes well-defined vibrational structure is observed at low temperature in glasses, polymeric films, or frozen solutions. The results of spectral fitting procedures have shown that, at low temperature, contributions appear in the spectra from medium-frequency  $(1000-1500 \text{ cm}^{-1})$  ring-stretching  $\nu$ (polypyridine) modes and from lower-frequency modes probably (Os-N) in character. At higher temperatures the vibrational structure is not observed due to thermal broadening. Emission band maxima and full bandwidths at half-height for the various emissions are presented in Table I. From the data, small but discernible shifts in emission band maxima are observed as the counterion is varied.

The completeness of ion pairing at room temperature in CH<sub>2</sub>Cl<sub>2</sub> solution was demonstrated in two ways. First, emission spectra and lifetimes of the Os(phen)<sub>3</sub><sup>2+</sup> salts were recorded at room temperature in propylene carbonate. Propylene carbonate has a high dielectric constant ( $D_s(25 \, ^\circ\text{C}) = 65$ ) compared to dichloromethane ( $D_s = 9$ ) and ion pairing is expected to be far less complete. As expected, in the concentration range used here, emission spectra and lifetimes in propylene carbonate showed little or no variation with counterion in marked contrast to dichloromethane. Secondly, the emission spectra of [Os(phen)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> and [Os(phen)<sub>3</sub>]Cl<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> were recorded in the presence of added [N(*n*-Bu)<sub>4</sub>](PF<sub>6</sub>) or [N(*n*-Bu)<sub>4</sub>]Cl. In neither case was there a shift in emission band maxima with added counterion up to 0.1 M suggesting that ion pairing was complete in the absence of added counterion.

It is possible to demonstrate the existence of specific ion pairing. Upon addition of  $[N(n-Bu)_4]Br$  (0.01 M) to a solution containing  $[Os(phen)_3](BPh_4)_2$  (0.2 mM), the emission maximum shifted from the value characteristic of the BPh<sub>4</sub><sup>-</sup> salt (696 nm) to the value for the Br<sup>-</sup> salt (714 nm). Values obtained for excited-state lifetimes and  $\ln k_{\rm nr}$  (=  $\ln (1/\tau)$ ) for the various salts are also included in Table I.

#### Discussion

In order to assess the role and possible origin of specific anion effects on nonradiative decay we have made emission and lifetime measurements on a series of salts of the complexes  $Os(phen)_3^{2+}$  and  $Os(4,4'-Ph_2phen)_3^{2+}$  in dichloromethane. The independence of emission energies and lifetimes in the presence of added counterions of the same type suggests that under our conditions ion pairing is complete in dichloromethane solution.

The choice of the Os(II)-polypyridyl complexes was dictated by a number of factors. Although the electronic structures are complicated, at room temperature excited-state properties are determined by a series of low-energy, Boltzmann populated MLCT states which have considerable triplet character and which behave kinetically as a single state. Because of the absence of low-lying dd excited states, the complexes are photochemically quite stable and show no tendency to undergo ligand-loss photochemistry. In addition, the fact that the complexes are weak emitters means that measurements of lifetimes can be used directly to obtain values for nonradiative decay rate constants,  $k_{nr}$ , without the necessity of measuring radiative  $\phi$  values.

From the data in Table I and Figure 1 it is evident that the effects of changes in counterions on either the emission energy or lifetimes of the excited states are relatively small. As a consequence, our ability to draw meaningful conclusions from the correlations discussed below relies on the statistical advantages inherent in the computer interfaced lifetime apparatus which was used to obtain the excited-state lifetime data. Note that each experimental lifetime point represents the average of 64 separate experiments which were used to estimate the uncertainties in Table I.

Applications of the Energy Gap Law. A quantitative basis for treating the observed anion effects on  $k_{\rm nr}$  is available based on the result in eq 4. By assuming that the properties of the acceptor vibrations and of  $S_{\rm M}$  and  $S_{\rm L}$  remain constant, noting that  $(k_{\rm B}T/\hbar\omega_{\rm M})(\gamma_0 + 1)^2 \approx 1$ , and assuming that the vibrationally induced electronic coupling term is also independent of changes in the counterion leads to

$$\ln k_{\rm nr} = \ln \beta_0' - \frac{\gamma_0 E_{\rm em}}{\hbar \omega_{\rm M}} + \frac{\chi_0}{\hbar \omega_{\rm M}}$$
$$\ln \beta_0' = \ln \beta_0 + S_{\rm L}(\omega_{\rm L}/\omega_{\rm M})(\gamma_0 + 1)$$
(5)

Equation 5 is in the form of the "energy gap law" which predicts a logarithmic relationship between the emission energy and  $k_{\rm nr}$ . In the series of experiments of interest here, the solvent remains constant and so the term  $\gamma_0/\hbar\omega_{\rm M}$  should also remain constant except for perhaps slight variations arising from differences between the polarization properties of the counterions and solvent molecules.

In Figure 2 are shown plots of  $\ln k_{nr}$  vs.  $E_{em}$  for the two complexes as the counterion is varied. Although there are inherent limitations in the accuracy of the data, the predicted linear relationship between  $\ln k_{nr}$  and  $E_{em}$  appears to be observed. As



TABLE II: Slopes and Intercepts (at  $E_{em} = 0$ ) from Plots of ln ( $k_{nr}$ ) vs.  $E_{em}$ 

	-1		
complex or complex series	slope, ev ·	ev	rei
$Ru(bpy)_3^{2+}$ (solvent variations)	-7.4 ± 0.7	$28.0 \pm 1.1$	4b
$Os(phen)L_4^{2+}$ (variations in L)	$-7.4 \pm 0.7$	$28.1 \pm 1.1$	23a
$[Os(phen)_3]X_2^a$	$-7.1 \pm 2.1$	$27.5 \pm 3.6$	this work
$[Os(4,4'-Ph_2phen)_3]X_2^a$	$-8.4 \pm 5.1$	29.2 ± 8.6	this work

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature.

shown from the comparisons in Table II, it is especially striking that the slopes and intercepts calculated for the lines in Figure 2 are within experimental error the same as those found earlier in experiments where the emission energy was varied either by varying the nonchromophoric ligand as in the series Os-(phen) $L_4^{2+4f,22,23}$  or by varying the solvent as found for Ru-(bpy) $_3^{2+4b}$ 

From the agreement obtained among the different types of experiments in Table II it can be concluded that the energy gap law is applicable in a general way to nonradiative decay for these complexes. Further, from the form of eq 5, such factors as the nature and contributions of the acceptor vibrations and of the vibrationally induced electronic coupling term remain relatively constant to variations in solvent, in surrounding counterions, and even in the nonchromophoric ligands.

As is also true for non-hydroxylic solvents, counterion effects have as their major origin their influence on the energy gap between the ground and excited states. In terms of excited-state dynamics and nonradiative decay, the critical role played by the energy gap is in its influence on the vibrational overlap or Franck-Condon factors for the acceptor vibrations. Equation 5 is a quantitative statement of the role of the energy gap from which it can be seen that in the high-temperature weak-vibrational coupling limit, the magnitude of the vibrational, overlap terms for the acceptor vibrations decrease with increasing energy separation. As a consequence, as the energy gap increases,  $k_{nr}$  decreases.

Microscopic Origin of the Anion Effect. Given what is known about excited-state structure in the Os complexes, it is possible to develop a qualitative model for the origin of the anion effect under conditions where ion pairing is complete. By now there is a sizable body of experimental evidence to suggest that in multiple chelate complexes like  $Os(phen)_3^{2+}$  the excited electron is localized on a single polypyridyl ligand at least on the vibrational time scale.<sup>14-16</sup> In fact, from the solvent dependence of absorption maxima for MLCT transitions in complexes like  $Ru(bpy)_3^{2+}$  and  $Os(bpy)_3^{2+}$ , it has been concluded that there is an induced dipole in the excited state and therefore that localization onto a single ligand occurs even in the optical excitation act.<sup>15</sup>

EPR line-broadening studies on related, singly reduced complexes like  $\operatorname{Ru}(\operatorname{bpy})_3^+$  and  $\operatorname{Fe}(\operatorname{phen})_3^+$  have shown that electron hopping among the various chelate rings is rapid at room temperature in acetonitrile solution.<sup>17a</sup> This is not a surprising result since it is expected for such electron transfer acts that intramolecular and solvent vibrational trapping should be relatively small. Presumably, intraligand electron transfer is also facile in the MLCT excited states, e.g.,  $(\operatorname{phen}^-)\operatorname{Os}^{III}(\operatorname{phen})_2^{2+*} \to (\operatorname{phen})-\operatorname{Os}^{III}(\operatorname{phen}^-)(\operatorname{phen})^{2+*}$ .

Given the  $D_3$  symmetry of the ground state in Os(phen)<sub>3</sub><sup>2+</sup>, the distribution of the two anions in the ion pairs in dichloromethane may involve preferred sites but is expected to be random with regard to the three ligands. On the other hand, the induced dipole



Figure 2. Plots of emission energy vs.  $\ln k_{nr}$  as the anions are varied in the series: (A)  $[Os(phen)_3]X_2$ , (b)  $[Os(4,4'-Ph_2phen)_3]X_2$ . For error limits note Table I.

in the excited state,  $(phen^{-})Os^{III}(phen)_2^{2+*}$ , provides an electrostatic basis for positioning of the anions on the side of the complex away from that ligand containing the excited electron.



In fact, such electrostatically based, preferred orientations of the counterions create a contribution to the trapping barrier to ligand to ligand electron transfer arising from anion translation. It is interesting to note that the dipole moments in the excited states  $(bpy)_2Ru^{III}(bpy^{-})^{2+*}$  and  $(bpy)_2Os^{III}(bpy)^{-})^{2+*}$  have been estimated to be  $14 \pm 6$  and  $13 \pm 6$  D from the absorption band solvent dependence study mentioned above.<sup>15</sup>

Just as for the excitation process associated with optical absorption, the deexcitation process associated with emission is rapid on the vibrational time scale ( $\sim 10^{-15}$  s). As a consequence, in the emission process the orientation of counterions before and after emission must be the same, which, as noted above, presumably involves a preferential orientation of the anions away from the ring holding the excited electron. Given the nature of the model, the most important factor contributing to anion-induced variations in the energy gap comes from variations in the differences in electrostatic interactions between the counterions and the charge distributions associated with the ground and MLCT excited states.

The factors involved are illustrated in the thermodynamic cycle shown in Scheme I which assumes a dielectric continuum for the solvent. In the cycle the anion-influenced emission energy,  $E_{em}$ ,

is related to the emission energy with no ion pairing,  $E^0_{em}$ , and the ion-pairing energies in the excited  $(\Delta E'_X)$  and ground states  $(\Delta E_X)$  by  $E_{\rm em} = E^0_{\rm em} + (\Delta E'_X - \Delta E_X)$ . The internal energy changes associated with the emission energies are negative quantities, a fact which is incorporated into this expression. The ionic charge is the same in the ground and excited states leading, to a first approximation, to a cancellation of anion-cation Coulombic terms in  $\Delta E_X$  and  $\Delta E'_X$ . However, a significant aniondipole term does exist for the excited state of the form,  $\Delta E'_{\rm X} \propto$  $-e|\mu|/R^2$ , where e is the unit electron charge,  $|\mu|$  the magnitude of the dipole moment, and R is the separation distance between the anion and the center of the dipole. There is no anion-dipole term in  $\Delta E_X$  because  $|\mu| = 0$  given the  $D_3$  symmetry of the ground state. The net effect is that the excited and ground states are expected to be stabilized about equally by Coulombic interactions with the surrounding anions but a further stabilization of the excited state occurs based on the anion-dipole interaction.

The analysis based on the thermodynamic cycle suggests that  $E_{\rm em}$  should vary as  $-1/(a + r_{\rm X})^2$  where  $R = a + r_{\rm X}$ ,  $r_{\rm X}$  is the radius of the ion, and a is determined by the properties of the excited-state dipole. There is insufficient information about the excited-state dipole and insufficient experimental data to test this prediction. However, it is evident from the data in Table I that  $E_{\rm em}$  does decrease as  $r_{\rm X}$ -decreases. In addition, although the sense of the changes in  $E_{em}$  with  $r_{X^-}$  are the same for Os(4,4'- $Ph_2phen)_3^{2+}$ , they are much less profound, consistent with the larger size of the cation and the concomittant increase in R.

The fact that correlations exist between the experimental emission energies and the anionic radii is significant in supporting an electrostatic origin for the variations in  $E_{em}$  and through  $E_{em}$ ,  $k_{nr}$ . It is important to note that correlations do not exist with other properties. In particular, a significant contribution to stabilizing the excited state and decreasing the energy gap could have been the extent of mixing of the outer sphere charge transfer (OSCT) excited state,  $Os^{II}(phen)_3^+$ , X, into the MLCT state. However,

if such an effect exists it must be of significantly less importance than the simple electrostatic effect identified here, since there is no obvious correlation of  $E_{\rm em}$  with ionization energies or redox potentials for the oxidation of the anions,  $X^- \rightarrow X + e^-$ .

### **Final Comments**

The results obtained here show that it is possible to account for the observation of specific anion effects based on the energy gap law and that the effects can be rationalized based on electrostatics. Even though the effects are small, the experimental observations provide a further experimental verification of the energy gap law and provide an understanding of the factors which determine excited-state lifetimes for MLCT excited states. With the acquisition of sufficient data it may be possible to turn the argument around and use excited-state lifetime measurements to obtain information concerning the surrounding medium.

It is important to realize that the experiments described here were carried out in fluid solution where environmental redistribution is rapid on the lifetime of the excited state. In media where translational and orientational correlation times are restricted, as in polymeric films, glasses, or solids, counterion effects may lead to some distinctively different features since the environment is constrained to be that of the ground state. If, for example, there is an anionic asymmetry, it may contribute to the trapping of the excited electron predominantly onto a single ligand even in complexes like  $Os(phen)_3^{2+}$  which have  $D_3$  intramolecular symmetry.

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**Registry No.** [Os(phen)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>, 75441-76-8; [Os(phen)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>, 14586-79-9; [Os(phen)<sub>3</sub>]Cl<sub>2</sub>, 73466-62-3; [Os(phen)<sub>3</sub>]Br<sub>2</sub>, 82313-96-0; [Os(phen)<sub>3</sub>](SCN)<sub>2</sub>, 82313-97-1; [Os(phen)<sub>3</sub>](BPh<sub>4</sub>)<sub>2</sub>, 88545-38-4;  $[Os(4,4'-Ph_2phen)_3](PF_6)_2$ , 94598-19-3;  $[Os(4,4'-Ph_2phen)_3](ClO_4)_2$ , 94598-20-6; [Os(4,4'-Ph2phen)3]Cl2, 94598-21-7; [Os(4,4'-Ph2phen)3]-Br<sub>2</sub>, 94598-22-8; [Os(4,4'-Ph<sub>2</sub>phen)<sub>3</sub>](SCN)<sub>2</sub>, 94598-23-9.

## Partial Molar Heat Capacities and Volumes of Transfer of Some Amino Acids and Peptides from Water to Aqueous Sodium Chloride Solutions at 298.15 K

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Partial molar heat capacities  $(\bar{C}_n^{\circ})$  and volumes  $(\bar{V}^{\circ})$  of some amino acids and peptides have been determined in water and aqueous sodium chloride solutions at 298.15 K with a Picker flow microcalorimeter and a vibrating-tube digital density meter. These data have been utilized to calculate the respective heat capacities and volumes of transfer for the amino acids and peptides from water to various molalities of sodium chloride solutions. The results show that heat capacities and volumes of transfer for the amino acids, peptides, and the peptide group are positive and may be regarded to result from the dominant interactions of sodium chloride ions with the charged centers of the amino acids and peptides. The results have been rationalized by a cosphere overlap model.

## Introduction

The study of the thermodynamic stability of the native structure of proteins has proved quite challenging and still remains a subject of extensive investigations.<sup>1</sup> Owing to the complexities arising from a direct thermodynamic study on proteins, investigations of the behavior of model compounds of proteins like amino acids and peptides in aqueous and mixed aqueous solvents make it easy to understand the factors governing the stability of the biopolymers.<sup>2,3</sup>

Salt solutions have large effects on the structure and properties of proteins including their solubility, denaturation, dissociation into subunits, and the activity of enzymes.<sup>4</sup> In the literature there are some reports<sup>1</sup> about the effect of various neutral salts on the

<sup>(1)</sup> Timasheff, S. N., Fasman, G. D., Eds. "Structure and Stability of Biological Macromolecules", Marcel Dekker: New York, 1969; Vol. 2, (a) Chapter 2, p 65; (b) Chapter 3, p 213.

<sup>(2)</sup> Rialdi, G.; Biltonen, R. In "International Review of Science", Physical Chemistry", Series 2; Skinner, H. A., Ed.; Butterworth: London, 1975; Vol. 10, pp 147-189. (3) Kauzmann, W. Adv. Protein Chem. 1959, 14, 1.

<sup>(4) (</sup>a) Von Hippel, P. H.; Schleich, T. In "Structure and Stability of Biological Macromolecules"; Vol. 2, Timasheff, S. N., Fasman, G. D., Eds.; Marcel Dekker: New York, 1969; p 417. (b) Jencks, W. P. In "Catalysis in Chemistry and Enzymology"; Mc-Graw Hill: New York, 1969; p 351. (c) Von Hippel, P. H.; Schleich, T. Acc. Chem. Res. 1969, 2, 257.