It seems evident from the kinetic studies, taken in conjunction with the equilibrium studies, that the decomposition of H_2O_2 does not involve a diperoxide or higher peroxide of monovanadate. At the higher peroxide concentrations of Table III, the diperoxide is the predominant product in solution and the decomposition proceeds slower than at the lower concentrations, where a major product is the monoperoxide. At even higher peroxide concentrations the decomposition reaction is almost stopped. Interestingly enough, under low peroxide concentrations similar to those utilized here, the decomposition of hydrogen peroxide is slowed or even stopped in the presence of small peptides, apparently because of the formation of a monoperoxovanadate/peptide complex. This aspect of the chemistry of peroxovanadates is of continuing interest.[20]

The decomposition observed here appears to be activated by both photochemical and thermal reactions, as the degradation is only slowed in the absence of light. The photochemical pathway for decomposition recently discussed[19] apparently does not operate efficiently under the conditions of the present study. The information here is not sufficiently detailed to provide a basis for a proposal for a mechanistic pathway. It is, however, perhaps worth noting that the results obtained here do not rule out the possibility that the hydrogen peroxide decomposition is catalyzed by a diperoxodivanadate.

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Excited-State Acid–Base Chemistry of (α-Diimine)cyanotricarbonylrhenium(I) Complexes

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The excited-state acid–base photophysics of rhenium(I) complexes of the form LRe^{I}(CO)$_3$CN (L = 1,10-phenanthroline, 2,2′-bipyridine, and 4,7-dimethyl-1,10-phenanthroline) was investigated. The emitting state can be tuned from a metal-to-ligand charge-transfer type to π–π^* phosphorescence by varying the acidity, L, and temperature. This alteration of excited-state type results in large changes in emission spectra and lifetimes, which suggest use as environmental probes. In low-temperature glasses, site heterogeneity must be invoked to account for the luminescence decay data.

Introduction

Highly luminescent transition-metal complexes are currently being investigated for their practical applications in solar energy conversion and catalysis,[1] molecular probes,[2-4] and sensors.[5] The most frequently studied are Ru(II)L$_3^{2+}$ complexes, where L = 2,2′-bipyridine, 1,10-phenanthroline, and substituted derivatives. However, there is also interest in other d^6 or d^8 complexes as photosensitizers including Os(II), Ir(III), Mo(0), W(0), Pt(II), and Re(I) complexes.[2a,6,7] In some cases these metal sensitizers exhibit more desirable excited-state properties than their Ru(II) counterparts.

In this study, we were interested in the excited-state acid–base photophysics of rhenium(I) complexes of the form LRe^{I}(CO)$_3$CN, where L = 1,10-phenanthroline (phen), 2,2′-bipyridine (bpy), and 4,7-dimethyl-1,10-phenanthroline (Me$_2$phen).

In particular, we investigated the effects of protonation of the cyanide ligand by varying the acidity in methanol/sulfuric acid solutions. We found the excited-state acid–base characteristics of the LRe(CO)$_3$CN complexes to be very similar to those of Ru^{II}L$_2$(CN)$_2$ complexes. Earlier studies of the Ru(II) compounds indicated that the complexes are stronger acids in the excited state, and protonation can invert the order of the lowest MLCT and π–π^* excited states with radical changes in the luminescence properties.[8a,b] The Re(I) complexes exhibit solvent-insensitive MLCT emission bands, which blue shift with increasing acidity. Room-temperature emissions were typically MLCT in character although by suitable choice of α-diimine ligand and acidity, a strong component or even dominant π–π^* emission arose. Low-temperature (77 K) studies indicate emissions from two different types of electronic excited states for (Me$_2$phen)Re(CO)$_3$CN (even without acid) and for the other two complexes at high acid concentrations. One emission is a $^3(\pi-\pi^*)$ phosphorescence, and the other is an MLCT emission.

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Experimental Section

Materials. $LRe(CO)_3Cl$ was prepared from $Re(CO)_5Cl$ as described earlier[6d,9] by using a suitable α-diimine from G. Frederick Smith Chemical Co. Sodium cyanide (Allied Chemical) was reagent grade. High-purity solvents (dichloromethane, ethanol, and methanol) were from Burdick-Jackson Laboratories. Concentrated sulfuric acid (95.9 wt %) and concentrated hydrochloric acid (37.3 wt %) were reagent grade from Mallinckrodt. Deionized water was redistilled from alkaline $KMnO_4$ in an all-glass distillation apparatus.

Synthesis. $LRe(CO)_3CN$ complexes were prepared by refluxing about 75 mg of the appropriate chloro complex in 25 mL of a 1:1 ethanol/water mixture or pure water containing a 100-fold molar excess of NaCN. The reflux was carried out over 6 h under a nitrogen atmosphere in darkness. The product was purified by extraction with dichloromethane, since the $LRe(CO)_3CN$ complexes are only slightly soluble in water. The products were dissolved in CH_2Cl_2 and precipitated by addition to cold hexane. If needed, they were purified on alumina with CH_2Cl_2/CH_3CN eluent. Elemental analyses were satisfactory with $(phen)Re(CO)_3CN$ and $(bpy)Re(CO)_3CN$ having half a water of hydration while $Me_2phenRe(CO)_3CN$ was anhydrous.

Solution Preparation. The solutions of the complexes were typically made up in methanol or methanol concentrated sulfuric acid mixtures. Sulfuric acid concentrations were 0.0, 3.6, 7.2, 10.8, 14.4, 18.0, and 21.6 N. Low-temperature measurements used these solutions except for the 0 N solution, which used methanol/water (4:1 by volume); pure methanol does not glass at 77 K.

The sample solutions were refrigerated and kept in the dark to reduce decomposition under acidic conditions. When these precautions were used, the sensitizers were stable for at least 2 weeks even under the most acidic conditions. Absorption spectra were monitored before each experiment to detect any degradation. Decomposition was signaled by a slight red shift and a decrease in absorption intensity of the MLCT bands.

Spectral Measurements. Absorption and emission spectra were obtained on equipment described earlier.[10a] Quantum yields were determined as described earlier.[10b] All emission spectra were obtained from aerated solutions with an excitation wavelength of 330 nm. A Pyrex filter between the sample and the collecting monochromator eliminated second-order peaks. Room-temperature emission spectra were collected by using a 1-cm-pathlength quartz cuvette. Low-temperature (77 K) measurements were made by using a quartz liquid-nitrogen Dewar inserted into the sample chamber. All the $MeOH/H_2SO_4$ glasses fractured badly and exhibited broad, featureless, short-lived emission blanks in the ultraviolet region. All emission spectra were instrument and background corrected.

Excited-state lifetimes (τ's) were measured with a pulsed nitrogen laser nanosecond decay time system described earlier.[11] Room-temperature lifetimes were collected with the monochromator set to the emission maxima. At room temperature, single-exponential decays were observed and fit by linear least-squares methods to the semilogarithmic plots of intensity versus time.

For the low-temperature measurements, transients were signal averaged and recorded on a Tektronix 2221 digital oscilloscope and transferred to an AT class PC under control of a Turbo Pascal program. Low-temperature lifetimes were collected at two different wavelengths: one corresponding to an MLCT emission maximum and the other to the ligand phosphorescence. The monochromator band-pass was 16 nm.

At low temperature, the nonexponential luminescent decay curves were fit by nonlinear simplex least-squares methods[12] to a sum of two or three exponentials.

$$I(t) = \sum_{i=1}^{2\text{ or }3} K_i \exp(-t/\tau_i) \tag{1}$$

where $I(t)$ is the luminescence intensity at time t, and the K's and τ's are the preexponential weighting factors and excited-state lifetimes, respectively. All decays were typically fit over two decades of intensity change.

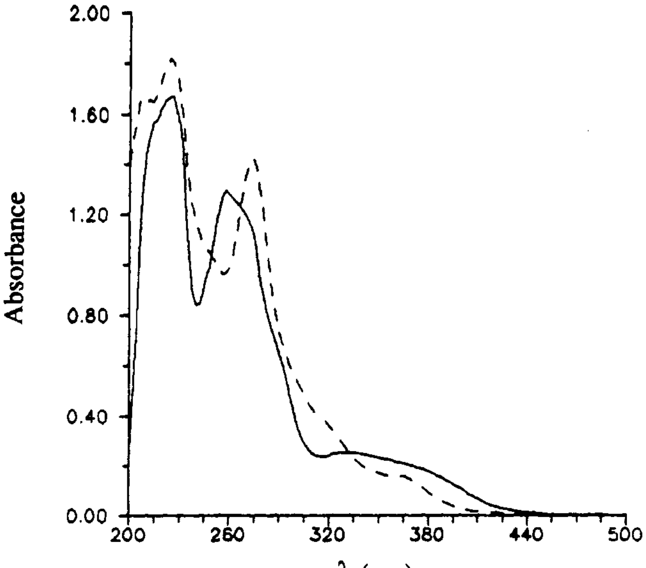

Figure 1. Absorption spectrum of $(phen)Re(CO)_3CN$ (50 μM) in methanol (—) without H_2SO_4 and 18 N H_2SO_4 (--).

Because multiexponential fits are notoriously unreliable, especially when the lifetimes are close to each other, we strove to reduce the number of parameters. This was done by assuming that a sample's τ's measured at long and short wavelengths were the same but the preexponential factors were different. For each acid concentration, our algorithm minimized the sum of the squares of the residuals (eq 2a) for the decays taken at both wavelengths; the preexponential factors and lifetimes were varied, but a common set of lifetimes was employed for both wavelengths. Our equations are

$$\chi_l^2 + \chi_s^2 \tag{2a}$$

$$\chi_l^2 = [I_l(t) - \sum_{i=1}^{2\text{ or }3} K_{li} \exp(-t/\tau_i)]^2 \tag{2b}$$

$$\chi_s^2 = [I_s(t) - \sum_{i=1}^{2\text{ or }3} K_{si} \exp(-t/\tau_i)]^2 \tag{2c}$$

where the subscripts l and s denote the long and short wavelengths, respectively. This seemed reasonable as we assumed that the unprotonated and protonated complexes were the only two species present. As we will show, the photophysics are more complicated.

These systems are complex since the emission spectra are functions of excitation wavelength. Such behavior can arise from multiple-ground-state species (e.g. ground-state heterogeneity) coupled with a failure of the multiple-excited-state species to equilibrate during their excited-state lifetime. To probe this behavior, we used the excitation spectra method described earlier.[13] For a sample, two uncorrected excitation spectra were measured with different emission wavelengths (λ_l and λ_s). $R(\lambda)$ is calculated from

$$R(\lambda) = E_s(\lambda)/E_l(\lambda) \tag{3}$$

where the E's are the emission intensities when exciting at λ and monitoring at the long or short wavelengths (l or s). Since the sample absorbance and excitation intensities are the same at each excitation wavelength, $R(\lambda)$ is related to the relative contributions of the different emission components. If there is no ground-state heterogeneity or equilibration in the excited state is rapid relative to the sample decay times, then R(λ) is wavelength independent. If there are multiple-ground-state species that fail to equilibrate in their excited states, $R(\lambda)$ varies with λ.

This procedure can be used without low-temperature absorption spectra or calibrating the excitation output. It compensates for solvent absorption, is insensitive to solution absorbance, and works with fractured glasses.

Results

Characterization. IR spectroscopy showed the $LRe(CO)_3CN$ complexes to all be facial isomers. This is consistent with ob-

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Table I. Emission Maxima (nm) vs Media for $LRe(CO)_3CN$

	emission max		
solvent	$(bpy)Re(CO)_3CN$	$(phen)Re(CO)_3CN$	$(Me_2phen)Re(CO)_3CN$
CH_2Cl_2	588	576	564
water	584	584	566
0.5 M HCl	586	584	566
methanol	586	577	560
12 M HCl	560	534	480 (sh), 508, 548 (sh)
36 N H_2SO_4	506	478 (sh), 498	472, 502, 536 (s), 576 (s)

Table II. Radiative Lifetimes for $LRe(CO)_3CN$ vs Acidity at 298 K

	τ_r, μs		
[acid], N	bpy	phen	Me_2phen
0.0	3.4	8.4	17.5
3.6	5.3	10.2	16.2
7.2	3.8	10.7	19.7
10.8	4.1	9.2	30.5
14.4	5.6	10.8	61.9
18.0	3.9	15.4	148.3
21.6	3.8	28.0	266.7

servations of other $LRe(CO)_3X$ complexes.[14] The solid Re(I) complexes are yellow, amorphous powders and are thermally and photochemically stable. They are soluble in most organic solvents except alkanes and are virtually insoluble in water. However, they are soluble in concentrated hydrochloric acid, which is convincing evidence of protonation.

Absorption Spectra. All the absorption spectra are similar. Figure 1 shows spectra for $(phen)Re(CO)_3CN$ in methanol and 18 N H_2SO_4/methanol. The spectra are dominated by low-energy MLCT transitions (320–380 nm) and higher energy ligand π–π^* transitions (<320 nm).[2a] A blue shift of the low-energy MLCT bands between 330 and 370 nm is observed when the cyano complex forms from the parent chloro complex. With increasing H_2SO_4 concentration, the MLCT bands blue shift. There are no isosbestic points.

Room-Temperature Emissions. Room-temperature solutions of the unprotonated $(L)Re(CO)_3CN$ complexes emit with a characteristic yellow luminescence that is blue shifted from the parent chloro compounds but has greater quantum efficiency. With the addition of acid, one could see the gradual blue shift of the emissions from yellow to green. Figure 2A shows spectra for $(phen)Re(CO)_3CN$ and Figure 2B shows spectra for $(Me_2phen)Re(CO)_3CN$. Spectra for $(bpy)Re(CO)_3CN$ were similar to those for $(phen)Re(CO)_3CN$.

The room temperature emission maxima in different solvents are shown in Table I. For $(phen)Re(CO)_3CN$ and $(Me_2phen)Re(CO)_3CN$, the 12 M HCl and 18 N H_2SO_4 spectra are very similar, and the concentrated H_2SO_4 spectra of the complexes resemble the phosphorescences of protonated phen and Me_2phen ligands, respectively.

Table II lists the radiative lifetimes for the complexes as a function of acidity derived from the observed lifetimes, τ_{obs}, and absolute luminescence quantum yields, ϕ, at different acidities.

$$\tau_r = \tau_{obs}/\phi \tag{4}$$

The radiative lifetimes for $(bpy)Re(CO)_3CN$ are short and essentially independent of acidity. The $(phen)Re(CO)_3CN$ lifetimes are somewhat longer and rise abruptly at the highest acidity. $(Me_2phen)Re(CO)_3CN$ starts at a high lifetime and increases rapidly with increased acidity.

Low-Temperature Emissions. Low-temperature emissions of the complex solutions ranged from bright green to bright blue depending on complex and acidity. Again, a blue shift was observed with increasing acidity.

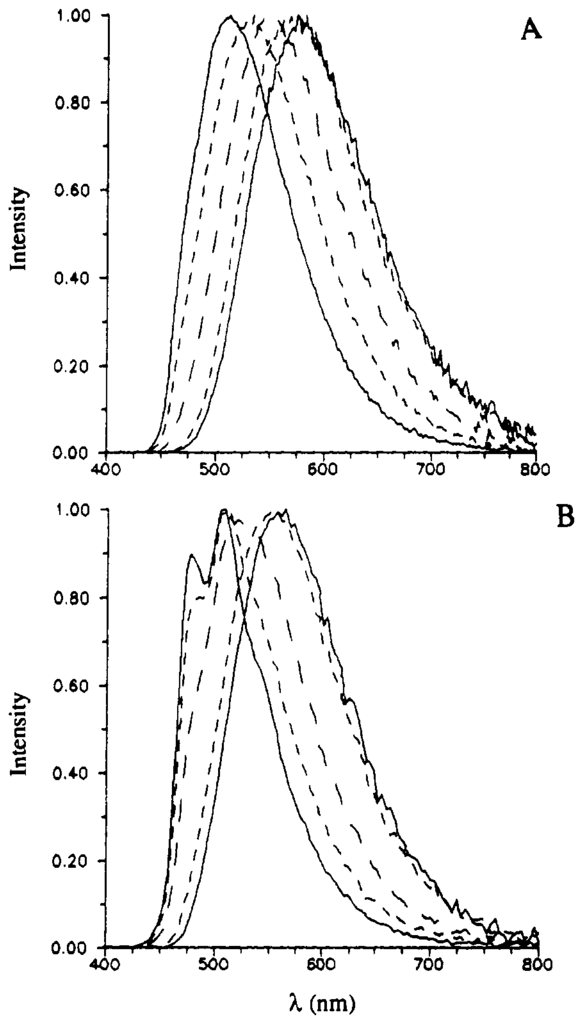

Figure 2. Room-temperature emission spectra of $(phen)Re(CO)_3CN$ (A) and $(Me_2phen)Re(CO)_3CN$ (B) as a function of acid concentration in methanol/H_2SO_4. Data are normalized to the same intensity. Acid concentration increases with increasing blue shift with normalities of 0, 7.2, 14.4, 18.0, and 21.6.

The low-temperature emission spectra of the complexes as a function of acidity are shown in Figure 3. As the acid concentration is increased, the emissions blue shift and acquire vibrational structure. The spectra in more acidic media bear striking resemblances to those of the $^3(\pi$–$\pi^*)$ phosphorescence spectra of $[Rh(phen)_3]^{3+}$, $[Rh(bpy)_3]^{3+}$, and $[Rh(Me_2phen)_3]^{3+}$.[15] On this basis, the structured emission features at higher acid concentrations are attributed to ligand $^3(\pi$–$\pi^*)$ phosphorescences.

For the emission lifetime measurements and $R(\lambda)$ determinations, one emission wavelength was selected to match the peaks of the ligand phosphorescence and another to match a region of strong MLCT emission that is relatively free of ligand phosphorescence. These were 458 and 540 nm for $(phen)Re(CO)_3CN$, 445 and 560 nm for $(bpy)Re(CO)_3CN$, and 464 and 568 nm for $(Me_2phen)Re(CO)_3CN$. The first of the wavelengths corresponds to the highest energy ligand $^3(\pi$–$\pi^*)$ emission peak.

Preliminary fits showed that except for $(bpy)Re(CO)_3CN$ at low acidities, all systems were not fit satisfactorily by single, or in most cases double, exponential fits. To satisfactorily fit both emission wavelengths with a common set of lifetimes required three exponentials. Three exponentials were even required for satisfactory fits to the $(phen)Re(CO)_3CN$ and $(Me_2phen)Re(CO)_3CN$ data at 0 N H_2SO_4.

In order to focus on the contributions from the different lifetime components, we calculated the fractional area associated with each lifetime component from

$$f_i = \frac{K_i\tau_i}{\Sigma K_i\tau_i} \tag{5}$$

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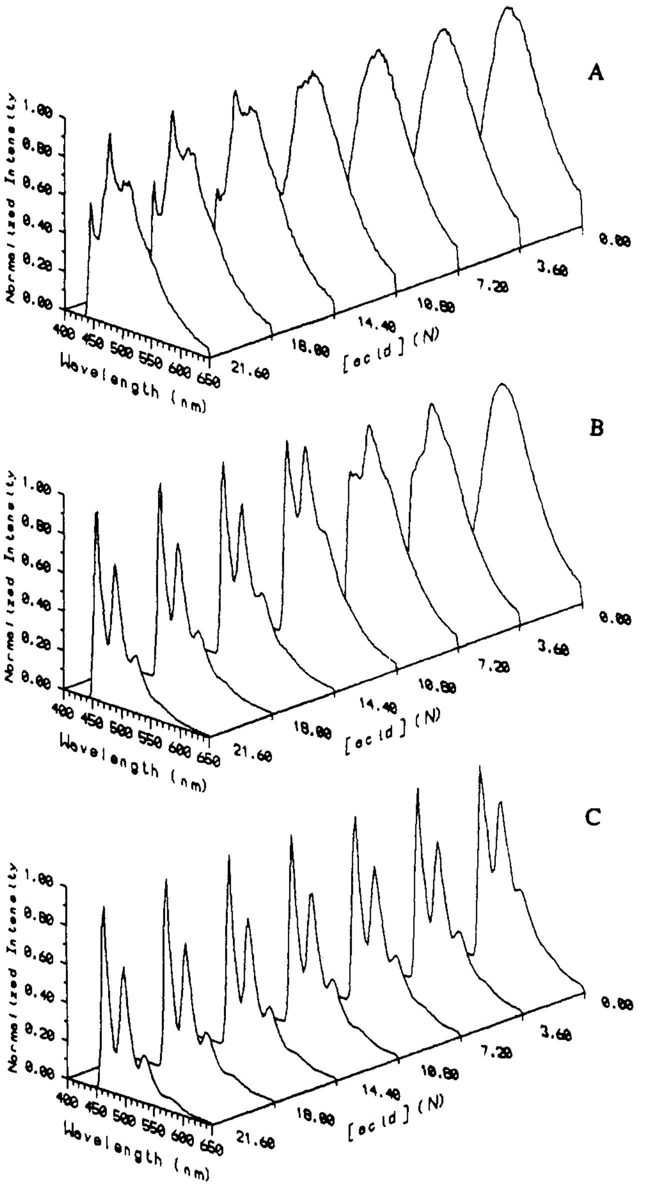

Figure 3. Low-temperature emission spectra of $LRe(CO)_3CN$ as a function of acidity: (A) L = bpy; (B) L = phen; (C) L = Me_2phen. Excitation was at 330 nm.

where f_i is the fractional contribution to the total emission for each component.

Figure 4 shows f_i data for $(phen)Re(CO)_3CN$ as a function of acidity at both monitoring wavelengths. There are three components: a very short-lived one, an intermediate one, and a long-lived one. At both monitoring wavelengths, the contribution from the short-lived component decreases with increasing acidity while the longest lived component increases its contribution. Further, the long-lived component has the greatest contribution at the short emission wavelength, while the short-lived component makes the strongest contribution at the longer wavelength. Similar results were obtained for $(bpy)Re(CO)_3CN$ and $(Me_2phen)Re(CO)_3CN$.

In order to discern more clearly the trend in relative component contributions, we present the mean lifetime for each system given by

$$\langle \tau_M \rangle = \frac{\Sigma K_i \tau_i^2}{\Sigma K_i \tau_i} \qquad (6)$$

Figure 5 shows a plot of the $\langle \tau_M \rangle$ for all three complexes as a function of acidity.

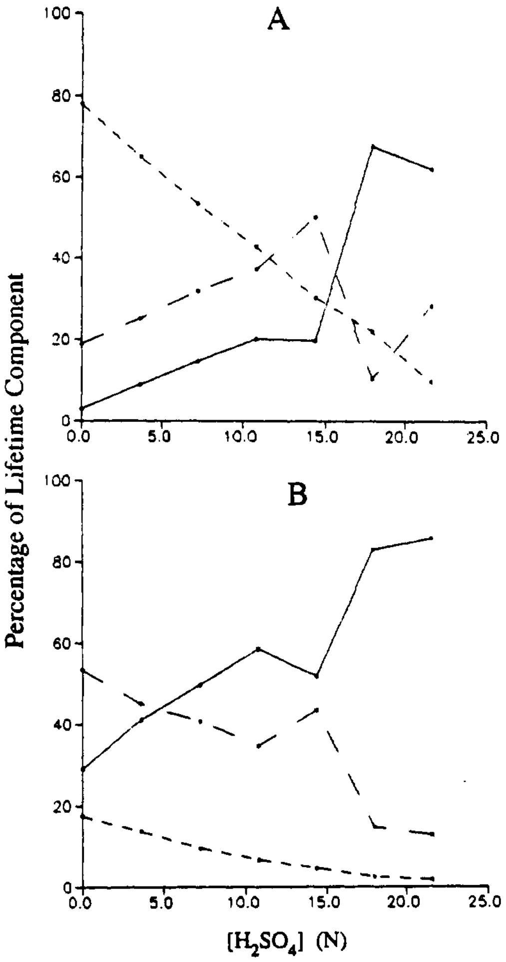

Figure 4. Percentage of short-lived (--), intermediate-lived (— —), and long-lived (—) components for $(phen)Re(CO)_3CN$ as a function of acidity and monitoring wavelength: (A) short monitoring wavelength; (B) long monitoring wavelength.

In view of the complex decay curves, a heterogeneous distribution of emitters in terms of chemical composition, states, and environmental sites seems a distinct possibility. This is supported in Figure 6, which shows $R(\lambda)$'s for $(phen)Re(CO)_3CN$ at both 0 and 21.6 N sulfuric acid concentrations. Similar results were obtained for $(Me_2phen)Re(CO)_3CN$. At zero or low acidity, $R(\lambda)$ is quite dependent on excitation wavelength. Thus, even at 0 N acidity, more than one emitter is probably present. For $(Me_2phen)Re(CO)_3CN$ at the highest acidity, the heterogeneity is largely suppressed. For $(bpy)Re(CO)_3CN$, there was no obvious heterogeneity at 0 N acid, but significant heterogeneity was observed for acidified solutions.

Solvent Effects. MLCT transitions on complexes with permanent dipole moments are frequently highly solvent sensitive. Since altering the media from 0 to 21.6 N H_2SO_4 represented a radical change in solvent environment, changes in emission and absorption properties irrespective of protonation were possible. The emission spectra of the $LRe(CO)_3CN$ are virtually insensitive to solvent (Table I). Only in highly acidic media are there appreciable emission shifts attributed to protonation; in the very highly acidic media the emission arises from the protonated form of the complexes.

For the 0.5 M HCl, the emissions are the same as for pure water. This is due to a rapid excited-state deprotonation to form the deprotonated excited complex. In the highly acidic media, the excited-state equilibrium favors the protonated form and large emission changes arise from emission of the protonated forms.

Discussion

These systems are complicated by the possible existence of both ground- and excited-state protonation of the complexes as well as solvent perturbation of the state energies. Protonation of –CN

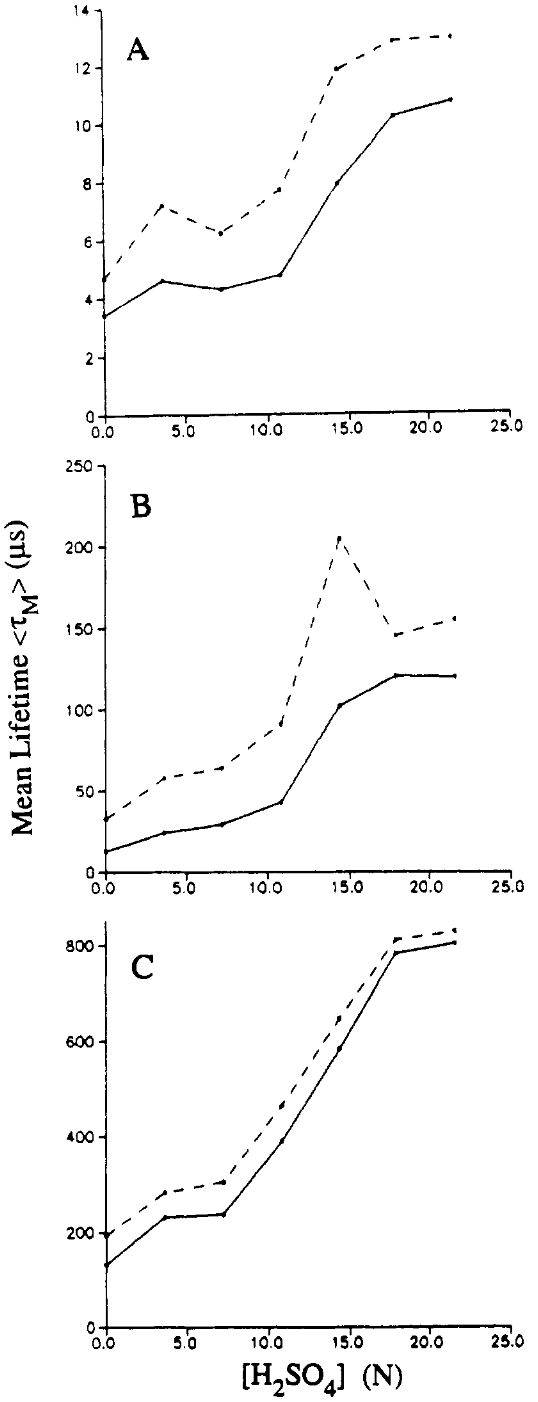

Figure 5. $\langle\tau_M\rangle$ for $LRe(CO)_3CN$ as a function of acidity and monitoring wavelength for short-lived (--) and long-lived (—) species: (A) L = bpy; (B) L = phen; (C) L = Me_2phen.

is well-known for $RuL_2(CN)_2$ complexes,[8a] and we assume an analogous reaction here as shown in Scheme I.

Scheme I

$$LRe(CO)_3CN + H^+ \rightleftharpoons LRe(CO)_3CNH^+$$

If the protonation-deprotonation is fast compared to the excited lifetime, then the decay curves will be single exponentials; there are multiple decays with slow equilibration. We discount the possibility of direct protonation of the α-diimine ligand at our relatively low acidities. Further, this has never been observed in M(α-diimine)$_3$ complexes.

There is direct evidence that protonation of the Re(I)-cyanide complexes is taking place in acid solutions. The compounds are virtually insoluble in water, yet the $LRe(CO)_3CN$ species dissolve readily in both concentrated sulfuric and hydrochloric acids.

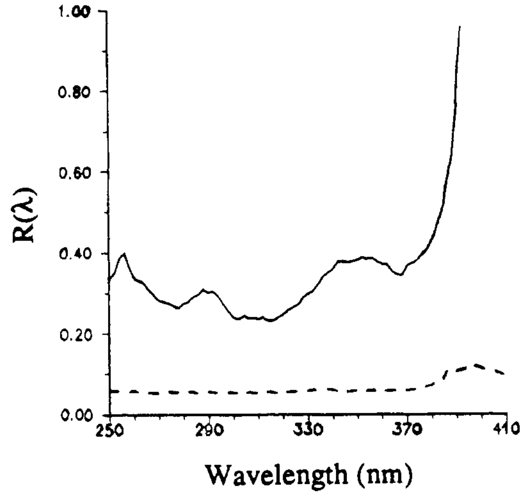

Figure 6. $R(\lambda)$ for (phen)$Re(CO)_3CN$ at 77 K as a function of $[H_2SO]_4$: (--) 0 N; (—) 21.6 N. Although not obvious for the 0 N data because of its amplitude, there is a very large fractional increase in R for long excitation wavelengths.

The blue shift on acidification is also consistent with protonation. A blue shift is a consequence of the stabilization of the t_2 metal orbitals on protonation of the -CN ($-CNH^+$). This effect is well-known from the protonation of $RuL_2(CN)_2$ (L = phen and bpy).[8] Similarly, substitution of isonitriles (-CNR) for -CN's (e.g., $RuL_2(CNR)_2$ and $RuL(CNR)_4{}^{2-}$) stabilizes the t_2 level.[16] The alkyl group on the NC serves a similar function to the proton. Both the $CH_3{}^+$ and H^+ serve the function of withdrawing electron density from the CN- group, thus, making it a better back-bonder. This stabilization of the t_2 level on protonation can raise the MLCT state above the π-π^* state and convert an MLCT emission of the parent -CN complex into a ligand-localized phosphorescence.

In the 0.5 M HCl media, the emission clearly arises from the unprotonated form of the complex, which shows that the equilibria of Scheme I lies well to the left and is established quickly on the time scale of the emission decay. This is analogous to that observed for $RuL_2(CN)(CNH)^+$ and $RuL_2(CNH)_2{}^{2+}$ at room temperature under conditions of moderate acidity (≤3 N H_2SO_4). However, in the much more acidic 12 M HCl, the large emission shifts for (phen)$Re(CO)_3CN$ and (Me_2phen)$Re(CO)_3CN$ versus the less acidic or pure water media leaves no doubt that the protonated forms of the complex are emitting. Thus, in 12 M HCl and the methanol/sulfuric acid media, the equilibrium is driven to the right in Scheme I. For 12 N HCl, the emission maxima falls between that of $MeOH/H_2SO_4$ mixtures of 0.58 and 0.67 weight fraction of H_2SO_4, and thus, they appear to have similar acidity.

The single exponential decays at room temperature are a result of rapid equilibration in fluid solution. The multiexponential decays at 77 K are probably partially a result of the solvent rigidity, which hinders rapid equilibration.

Assignments. At room temperature, the broad structureless emissions of (bpy)$Re(CO)_3CN$ and (phen)$Re(CO)_3CN$ are typical of MLCT emissions of Re(I) complexes.[2a] Their radiative lifetimes are also typical of predominantly MLCT emissions. On this basis, we assign the room-temperature emissions of (bpy)$Re(CO)_3CN$ and (phen)$Re(CO)_3CN$ as MLCT in character.

At room temperature, (Me_2phen)$Re(CO)_3CN$ shows a broad structureless MLCT emission at low acidity, but at the higher acid concentrations, the emission blue shifts, sharpens, and acquires vibrational structure. The radiative lifetime also increases sharply as the new structure is acquired. The structure is similar to that of the 77 K emission. The 77 K emission is assigned to a ligand phosphorescence by its similarity with the ligand phosphorescence of $Rh(Me_2phen)_3{}^{3+}$. The similar structure at 298 and 77 K shows

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(16) Indelli, M. T.; Bignozzi, C. A.; Marconi, A.; Scandola, F. *J. Am. Chem. Soc.* **1988**, *110*, 7381.

that the room-temperature emission at high acidities is largely a ligand-localized phosphorescence. Thus, at room temperature, the emission shifts from predominantly MLCT in character to a predominantly π–π^* phosphorescence on acidification.

At 77 K, the character of the emission depends on the complex and acidity. At 77 K, there are two discernible emission components: a broad structureless one and a highly structured one. At 0 N acid, the structured emission is essentially nonexistent for $(bpy)Re(CO)_3CN$ and $(phen)Re(CO)_3CN$ while $(Me_2phen)Re(CO)_3CN$ shows significant amounts of both structured and broad-band emissions. The structured emission grows in with increasing acidity and is the dominant emission at 21.6 N for both $(phen)Re(CO)_3CN$ and $(Me_2phen)Re(CO)_3CN$. By analogy with a variety of Re(I) complexes, we assign the broad structureless emission to an MLCT emission. The striking similarity of the highly structured emission with the ligand-localized π–π^* phosphorescences of $Rh(bpy)_3^{3+}$, $Rh(phen)_3^{3+}$, and $Rh(Me_2phen)_3^{3+}$ leave no doubt that the structured emissions are ligand-localized phosphorescences of the coordinated ligands.

State Tuning. All of the emission results can be explained on the basis of the original state orderings and subsequent tuning of the energies of the MLCT and π–π^* triplet states by temperature and acidity. The initial relative position of the lowest MLCT and π–π^* triplet is controlled in part by the α-diimine ligand. For the series of ligands bpy, phen, and Me_2phen, the π–π^* triplet state red shifts while the lowest MLCT state blue shifts. Compare the first vibronic ligand phosphorescence peaks of the $LRe(CO)_3CN$ of 445 (L = bpy), 458 (L = phen), and 464 nm (L = Me_2phen). If the MLCT state is lowest, these shifts have the effect of reducing the separation between the MLCT state and π–π^* triplet states or even inverting the states.

The complexes are protonated when acid is added. Protonation of –CN in α-diimine complexes is known to blue shift the energies of the MLCT states while leaving the π–π^* triplet state relatively unaffected.[8a,b] This is shown for the 298 and 77 K data in Figure 7. Blue shifting the MLCT state has the effect of increasing the component of π–π^* phosphorescence. In the extreme case of state inversion, the emission can change from an MLCT phosphorescence to a predominantly ligand-localized one.

We turn now to the changes in emission characteristics with temperature. All of the behavior can be accounted for in terms of the sensitivity of MLCT state energies to solvent properties and the rates of solvent relaxation relative to the emission decay time. The MLCT state sensitivity arises from the significant change in dipole moment or redistribution of electron density that accompanies MLCT excitation. Because of this change, the MLCT excited state formed initially is nonequilibrated with respect to solvent orientation and internal geometry. At room temperature, the complex and environment can relax to the thermally equilibrated excited (*thexi*) state on a time scale that is short compared to the decay time. Equilibration causes a significant drop in the MLCT state energy. In a rigid glass at 77 K, formation of the *thexi* state cannot occur during the excited-state lifetime, and the emission will arise from the higher energy unequilibrated form. In contrast, the π–π^* states in our systems do not involve large changes in dipole moment, and the ligand-state energies are largely insensitive to solvent and to relaxation processes following excitation. Dipole moment changes on excitation are not required to produce significant drops in MLCT states on equilibration. There is a significant blue shift in $Ru(bpy)_3^{2+}$ on going from a fluid to a rigid low-temperature glass.

We now apply these concepts to our specific complexes. Correlating these factors with observed spectroscopy leads to the state diagrams of Figure 7. Specifically, we show that the changing character of the emissions (Figures 2 and 3) with temperature and acidity is entirely consistent with the diagrams of Figure 7.

First consider the room-temperature data. All the spectra show blue shifts on acidification and, except for $(Me_2phen)Re(CO)_3CN$ at the highest acidity, exhibit MLCT emissions. Even on protonation the relaxed MLCT states still lie below the π–π^* triplet states. The one exception is the $(Me_2phen)Re(CO)_3CN$ where the MLCT state starts closer to the π–π^* triplet state and protonation raises the MLCT state to near degeneracy or above the π–π^* triplet state.

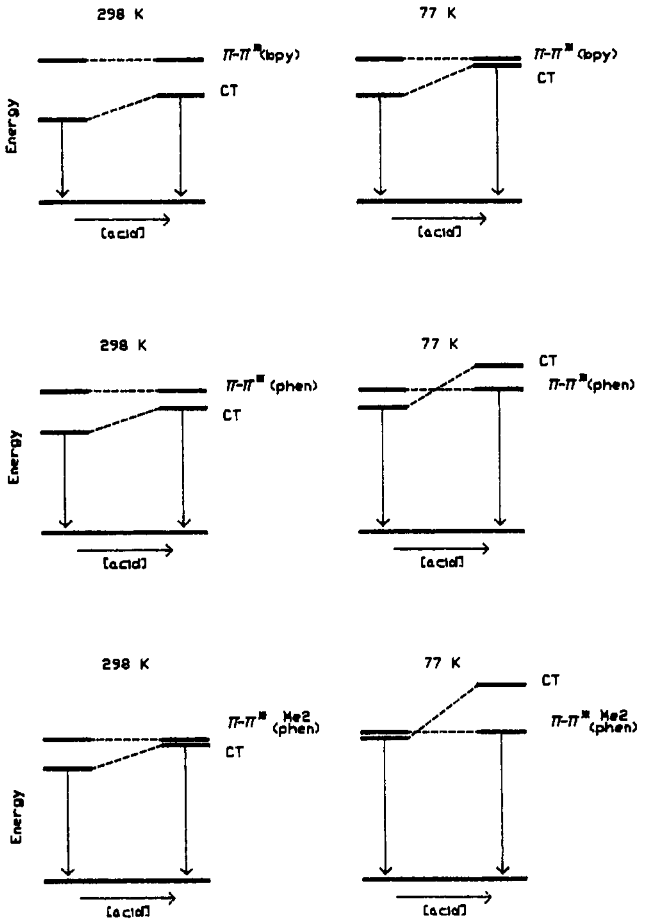

Figure 7. State diagram for $LRe(CO)_3CN$ complexes as a function of acidity, L, and temperature.

At 77 K, protonation blue shifts the emissions (Figure 3). At low acidities the emissions are predominantly MLCT except for $(Me_2phen)Re(CO)_3CN$. The component of highly structured ligand phosphorescence increases with increasing acidity with $(bpy)Re(CO)_3CN$ showing significant ligand emission at 21.6 N and $(phen)Re(CO)_3CN$ showing essentially pure ligand emission at 21.6 N. $(Me_2phen)Re(CO)_3CN$ shows only a small component of MLCT emission even at 0 N acid and none at 21.6 N acid.

Similar to the effects seen at 298 K, these results are a consequence of the raising of the MLCT state energy on protonation, which allows a greater contribution of ligand emission. The greatly increased ligand emission components relative to the 298 K results arises from the rigidity of the environment that prevents relaxation of the MLCT state and keeps it at higher energy relative to the ligand π–π^* triplet state. The increasing ligand emission component on going from $(bpy)Re(CO)_3CN$ to $(phen)Re(CO)_3CN$ to $(Me_2phen)Re(CO)_3CN$ arises from the increasing initial energy of the MLCT state relative to the π–π^* triplet state.

The increasing ligand contribution to the emission on increasing acidity and changing the ligand from bpy to phen to Me_2phen is supported by the lifetime results. Consider the phen data of Figure 4. We assign the short-lived component to the MLCT emission and the long-lived component to the ligand phosphorescence. The fraction of the short-lived emission is largest at the longer wavelength (MLCT emission) and smallest at the short wavelength (ligand emission) while the long-lived contribution is greatest at the short wavelength. Increasing the acidity decreases the contribution of the short-lived component and raises that of the long-lived component at both wavelengths. The intermediate lifetime component has a lifetime that varies from 20 to 60 μs and shows a wavelength dependence similar to that of the short-lived MLCT emission. Similar results were obtained for the other two complexes.

Figure 5 further supports this picture. The $\langle\tau_M\rangle$'s increase monotonically with increasing acidity and on going from bpy to phen to Me_2phen. In addition, the $\langle\tau_M\rangle$'s increase when the monitoring wavelength is changed from the peak of the MLCT emission to the wavelength of the ligand emission. The purest ligand emission is from (Me_2phen)Re(CO)$_3$CN where the 800-μs lifetime approaches that of organic phosphorescences. The shorter $\langle\tau_M\rangle$'s for (bpy)Re(CO)$_3$CN and (phen)Re(CO)$_3$CN arise from the greater MLCT emission contribution to the total emission.

Site Heterogeneity. Our lifetime results clearly show that the simple two-component model of Scheme I is an over simplification at 77 K. Such a model requires only two lifetimes; however, at least three and sometimes four components are required to provide satisfactory fits. Even the single component systems of (phen)-Re(CO)$_3$CN and (Me_2phen)Re(CO)$_3$CN in methanol-water glasses require two lifetimes for the fit. Further, the $R(\lambda)$'s for all complexes are not flat at 0 N acid, indicating ground-state heterogeneity.

The most probable explanation is environmental site heterogeneity. In the rigid glasses, the polar molecules examined here can probably exist in different environments; due to the sensitivity of MLCT emissions to environmental effects, several lifetimes or a range of lifetimes can exist. This gives rise to our complex decay kinetics. For this reason, one should not make too much of our lifetimes and preexponential factors. Our fitting procedure represents this range or distribution of lifetimes as a discrete three-component fit. While the long and short lifetime contributions probably give reasonable estimates of the wings or limit contributions, the intermediate lifetime is probably an adjustable parameter that gives some average over the range and amplitude of lifetimes actually present.

Low-energy excitation favors MLCT emission regardless of ligand or acidity. In Figure 6, the increase in $R(\lambda)$ at long excitation wavelengths demonstrates increased CT emission. We attribute this to photoselection of sites that have the lowest MLCT states in the molecule, which then give predominantly, or exclusively, MLCT emissions.

Conclusion

As with previously studied Re(I) sensitizers, complexes of the form LRe(CO)$_3$CN [L = Me_2phen, phen, bpy] investigated in this study were found to exhibit MLCT and π–π^* transitions in their absorption and emission spectra. Excited-state acid–base studies of these compounds in highly acidic methanol/sulfuric acid media indicate that protonation of the cyanide ligand is taking place. Further, our results indicate that spectra and lifetime changes are principally due to protonation of the CN and that ordinary solvatochromism plays at best a minor role. At room temperature, emissions from only MLCT transitions (associated with the unprotonated species of each complex) were observed except under the most acidic conditions; this indicates that the complexes are stronger acids in the excited state than in the ground state. At low temperature (77 K), emissions from both the unprotonated and protonated species were observed, as indicated by $^3(\pi-\pi^*)$ vibrational structure in the emission spectra and multicomponent fits of the luminescence decay curves. The low-temperature emission data also suggest that the degree of protonation is increasingly advanced on going from (bpy)Re(CO)$_3$CN to (phen)Re(CO)$_3$CN to (Me_2phen)Re(CO)$_3$CN.

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Hexanuclear Homo- and Heterobridged Ruthenium(II) Polypyridine Complexes: Syntheses, Absorption Spectra, Luminescence Properties, and Electrochemical Behavior

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By use of the "complexes as ligands" strategy, the trinuclear complexes $\{Ru[(BL_a)Ru(bpy)_2]_2Cl_2\}(PF_6)_4$ (**5**, BL_a = 2,3-dpp; **6**, BL_a = 2,5-dpp) have been synthesized from the reaction of $RuCl_3 \cdot 3H_2O$ with $[Ru(bpy)_2(2,3\text{-dpp})](PF_6)_2$ and $[Ru(bpy)_2(2,5\text{-dpp})](PF_6)_2$, respectively (bpy = 2,2′-bipyridine; dpp = bis(2-pyridyl)pyrazine). Reaction of two units of **5** or **6** with the 2,3-dpp or 2,5-dpp bridging ligands has led to the formation of four hexanuclear complexes (**1**–**4**) of general formula $\{[(bpy)_2Ru(BL_a)]_2Ru(BL_b)Ru[(BL_a)Ru(bpy)_2]_2\}(PF_6)_{12}$, where BL_a = BL_b = 2,3-dpp (**1**), BL_a = BL_b = 2,5-dpp (**2**), BL_a = 2,3-dpp and BL_b = 2,5-dpp (**3**), and BL_a = 2,5-dpp and BL_b = 2,3-dpp (**4**). Such hexanuclear compounds exhibit extremely intense absorption bands in the UV region (λ_{max} = 283 nm, ϵ_{max} of the order of 2×10^5 M^{-1} cm^{-1}), which can be assigned to ligand-centered transitions, and intense bands in the visible region (λ_{max} between 540 and 582 nm, ϵ_{max} of the order of 5×10^4 M^{-1} cm^{-1}), which can be assigned to metal-to-ligand charge-transfer transitions. Complexes **1**–**4** are luminescent both in rigid matrix at 77 K and in fluid solution at 298 K. Luminescence originates from the lowest (formally triplet) metal-to-ligand charge-transfer excited state. The emission spectra and lifetimes are approximately the same for **1** and **3** and for **2** and **4**. For **1** and **3** emission occurs at higher energies and exhibits a longer lifetime compared to **2** and **4** (770 vs 810 nm and 54 vs 42 ns, in acetonitrile solution at 298 K). These results, as well as a comparison with the behavior of analogous di- and trinuclear compounds, indicate that in all cases luminescence takes place from the peripheral $(bpy)_2Ru(BL_a)^{2+}$ chromophoric units. Corrected excitation spectra have shown that energy transfer from the central chromophoric units to the peripheral ones takes place with ~100% efficiency. In electrochemical experiments, the four peripheral metal ions are oxidized at about the same potential (~+1.4 V, vs SCE), whereas oxidation of the two inner metal ions cannot be observed in the potential window examined (<+2.0 V). Several reduction overlapping waves are present beginning at about −0.5 V.

Introduction

There is an increasing interest in luminescent and redox-reactive polynuclear metal complexes[2-4] because of their relevance for the design of photochemical molecular devices.[4-7] In several cases polynuclear complexes may be considered as supramolecular

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(2) The literature on this topic is too vast to be exhaustively quoted. For recent reviews, see refs 3 and 4.

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