Excited-State Acid-Base Reactions of Dicyanobis(2,2'-bipyridine)ruthenium(II) and Dicyanobis(1,10-phenanthroline)ruthenium(II)

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Abstract: Excited-state acid-base reactions of $RuL_2(CN)_2$ (L = bpy and phen where bpy = 2,2'-bipyridine and phen = 1,10-phenanthroline) were studied at room temperature and at 77 K. At room temperature (0.3 M < H^+ < 3 M), substantial amounts of HD^+ and H_2D^{2+} can coexist with D, but on excitation $^*HD^+$ and $^*H_2D^{2+}$ are such strong acids and they deprotonate so rapidly ($^*H_2D^{2+} \rightarrow {}^*HD^+ \rightarrow {}^*D$) that only the charge-transfer (CT) emission from *D is observed. These excited-state deprotonation reactions occur with 100% efficiency. At 77 K in highly acidic H_2SO_4-methanol glasses, emission from the protonated forms occurs. With $Ru(phen)_2(CN)_2$ and possibly with $Ru(bpy)_2(CN)_2$, the lowest CT state of H_2D^{2+} is raised above the lowest ligand localized $^3(\pi-\pi^*)$, and the emission changes to a $^3(\pi-\pi^*)$ phosphorescence. This appears to be the first case of inversion of excited-state type in metal complexes on undergoing a protonation reaction.

Excited-state acid-base reactions of organic molecules have long been known and studied by luminescence methods.[1,2] In spite of the enormous recent interest in luminescent transition metal complexes,[3-6] however, information on their excited-state acid-base properties is still quite limited.[7-9] Also, in view of the successful utilization of excited-state acid-base reactions in organic laser dye systems, detailed information concerning such processes in metal complexes could prove helpful in their utilization in laser dye systems.

Only recently have emission methods been applied to studying the excited-state acid-base properties of transition-metal complexes. The first definitive direct evidence for an excited-state acid-base reaction for a transition-metal species is our study of the greatly enhanced excited-state acidity of the protonated forms of dicyanobis(2,2'-bipyridine)ruthenium(II), $Ru(bpy)_2(CN)_2$, in aqueous acid.[7] The two cyano groups are basic and under highly acidic conditions ($[H^+] \geq \sim 0.2$ M) solutions contain H_2D^{2+}, HD^+, and D in equilibrium (D = $RuL_2(CN)_2$). Emission from these acidified aqueous solutions, however, shows only the emission spectrum of *D, regardless of the concentration of $HClO_4$. Emission quenching by $[H^+]$ also shows non-Stern-Volmer behavior, but the luminescence quantum yields from *D are independent of whether H_2D^{2+}, HD^+, or D is excited in each mixture. These results are explained in terms of a rapid, complete deprotonation following excitation of the protonated species. Later, other workers saw simultaneous emissions from H_2D^{2+} and D where D is $[Ru(bpy)_2(4,4'-(HOOC)_2(bpy)]^{2+}$.[8]

We wish to report here additional studies on $Ru(bpy)_2(CN)_2$ and results for the similar dicyanobis(1,10-phenanthroline)ruthenium(II), $Ru(phen)_2(CN)_2$. These systems are unique in that inversion of the lowest charge transfer (CT) and ligand localized triplet ($^3(\pi-\pi^*)$) states occurs on protonation with a complete change in the emission character of the systems.

Experimental Section

Previously prepared $Ru(bpy)_2(CN)_2$[10] and $Ru(phen)_2(CN)_2$[11] were freshly purified by column chromatography on silica gel with methanol eluent. The materials used exhibited only a single spot on TLC (silica gel, methanol eluent) and exhibited the same ratio of the peak to trough absorbance in solution as previously obtained samples. Mallinckrodt concentrated acids were used without further purification; acid concentrations were checked by titration against tris(hydroxymethyl)aminomethane (Tham).

Absorption spectra were measured on a Cary Model 14 spectrophotometer. Emission lifetimes were measured with a microcomputer controlled sampling oscilloscope based boxcar integrator.[12] Excitation was with either a 1-kW Phase-R pulsed nitrogen laser[13] or a Molectron UV-14 400-kW nitrogen laser. The excitation beam was passed through a 1-cm aqueous solution filter of $CuSO_4{\cdot}5H_2O$ (100 g/L). With the Molectron laser, the emission wavelength was isolated with a Jobin-Yvon H10 holographic grating monochromator. Emissions were observed with an RCA 6342R photomultiplier tube. To reduce scattered stray light a 1-cm solution filter of saturated aqueous $NaNO_2$ was interposed between the sample and the monochromator. The laser pulse width (~10 ns) was sufficiently short that it could be treated as a δ function.

Emission and excitation spectra were obtained with the instrument partially described earlier[14] and shown schematically in Figure 1. Excitation spectra were corrected for spectral variations in the source intensity by means of a Rhodamine B quantum counter (5 g/L in methanol) which has a sensitivity which is flat to ±2% over the range of interest;[15] no corrections were applied for these small deviations. A single-beam method was employed. Without the sample in the excitation beam, the spectral distribution of the source was measured with the quantum counter. The quantum counter was masked and the sample excitation spectrum was measured using right-angle viewing. All sample optical densities were <0.1/cm. The spectral distribution of the source was then rechecked; the run was discarded if the two distributions did not agree within 5%. For low-temperature studies, a Pyrex optical Dewar was inserted into the sample chamber.

Samples for emission measurements were optically dilute (absorbance ≤ ~0.1/cm). For room temperature lifetime and intensity measurements, the solutions were bubbled with nitrogen to exclude quenching by dissolved oxygen. Reported emission spectra are uncorrected for detector response, although previous tests have shown the system to be relatively flat in response across the wavelength range studied.

Results

Room Temperature Results. Absorption spectra for the low-energy charge-transfer (CT) region for $Ru(phen)_2(CN)_2$ in water at different concentrations of $HClO_4$ are shown in Figure 2A. There is a strong blue shift on increasing acidity but no isosbestic points. These results are consistent with the two-step protonation of the CNs to form HD^+ and H_2D^{2+} as is observed for $Ru(bpy)_2(CN)_2$ where similar absorption changes with $[H^+]$ are seen.[7] Acidified solutions of $Ru(phen)_2(CN)_2$ and $Ru(bpy)_2(CN)_2$ all emitted with the characteristic orange spectrum of the parent unprotonated complex in pure water, although with reduced efficiency.

Corrected relative luminescence quantum yields, $\theta(\bar{\nu})$, for the mixtures were calculated from excitation spectra by

$$\theta(\bar{\nu}) = \frac{O(\bar{\nu})}{GI(\bar{\nu})\{1 - \exp[-2.303A_{\bar{\nu}}]\}} \qquad (1)$$

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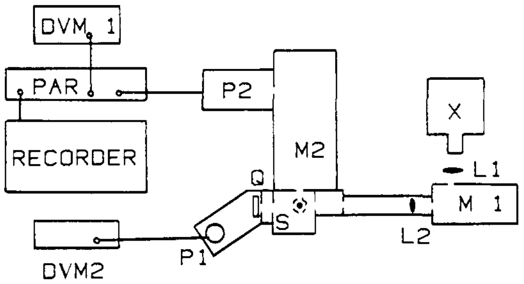

Figure 1. Schematic diagram of spectrofluorimeter used: X, 1000-W xenon arc lamp; L1, Pyrex collection lens; M1, 0.25 M Bausch and Lomb grating monochromator; L2, achromatic lens; S, sample compartment; Q, 1-cm path length Rhodamine B quantum counter; P1, P2, red sensitive PMTs; M2, Perkin-Elmer Model 99 monochromator with a glass prism; PAR, Princeton Applied Research Model 121 lock-in amplifier; DVM1, DVM2, digital voltmeters.

where $O(\bar{\nu})$ is the observed intensity of emission of *D at excitation energy $\bar{\nu}$ (observed at the emission maximum), $I(\bar{\nu})$ is the relative excitation source intensity obtained from the Rhodamine B quantum counter, and $A_{\bar{\nu}}$ is the sample absorbance in the 1-cm measurement cell. Since the solution absorbances were small (<0.1/cm), corrections for deviations from the optically dilute limit were less than 5% and thus accurately accounted for by eq 1. The scale factor G was chosen to give $\theta(\bar{\nu})$ an average value of unity across the normalization region for the acid-free solution.

Figure 2C shows the corrected relative luminescence quantum yield vs. $\bar{\nu}$ for the $Ru(phen)_2(CN)_2$ solutions. The yield is based on the total absorbance of the solution and makes no assumption about the composition.

Very similar results in absorption, emission, and relative quantum yield vs. $\bar{\nu}$ for $Ru(bpy)(CN)_2$ have been reported elsewhere[7] and will not be duplicated here. It is noteworthy, however, that more recent measurements made with lower excitation intensities have eliminated the apparent slight decrease in quantum yield at longer wavelengths for the higher $[H^+]$ solutions of $Ru(bpy)_2(CN)_2$; this is consistent with our having attributed this decrease to photochemical decomposition.

All attempts to force emission from the excited states of the protonated forms of $Ru(bpy)_2(CN)_2$ at room temperature failed. In 12 M HCl or glacial acetic acid with added $HClO_4$, either no emission was detectable or only the orange one characteristic of the unprotonated $Ru(bpy)_2(CN)_2$ occurred.

To fully interpret the excitation spectra, the composition of the acidified solutions in terms of D, HD^+, and H_2D^{2+} was required. Although not exact, the following procedure gave reasonable results for the solution compositions vs. acid concentration.

First, we took advantage of the fact that at long enough wavelengths only D absorbs while HD^+ and H_2D^{2+} are transparent. This was shown by making plots of the fractional absorbance $(F_D(\bar{\nu}))$ of the solutions relative to the unacidified solution.

$$F_D(\bar{\nu}) = A_{\bar{\nu}}([H^+])/A_{\bar{\nu}}(0) \qquad (2)$$

where $A_{\bar{\nu}}([H^+])$ is the absorbance vs. $[H^+]$. At long enough wavelengths ($\lambda \geq 460$ nm for $Ru(bpy)_2(CN)_2$ and $\lambda \geqslant 450$ nm for $Ru(phen)_2(CN)_2$), $F_D(\bar{\nu})$ becomes independent of $\bar{\nu}$ for each acid concentration. Because the relative amounts of D, HD^+, and H_2D^{2+} vary with $[H^+]$, the independence of $F_D(\bar{\nu})$ with $\bar{\nu}$ at these longer wavelengths can only occur if D is the only significantly absorbing species. Therefore, at the longer wavelength $F_D(\bar{\nu})$ represents F_D, which is the fraction of complex present as free D.

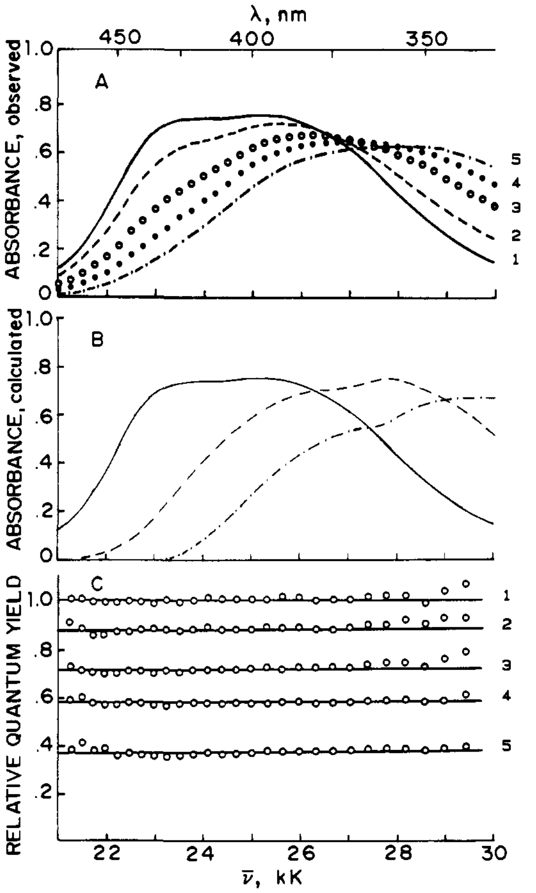

Figure 2. (A) Absorption spectra for $Ru(phen)_2(CN)_2$ in aqueous $HClO_4$ solutions (7.7×10^{-6} M in complex in a 10-cm path length cell). Acid concentrations for each curve are 0 (1), 0.24 (2), 0.72 (3), 1.20 (4), and 1.92 M (5). (B) Absorption spectra for $Ru(phen)_2(CN)_2$ (—) and calculated spectra for $[Ru(phen)_2(CN)(CNH)]^{+2}$ (---) and $[Ru(phen)_2(CNH)_2{}^{2+}$ (-····-). (C) Corrected relative luminescence yields vs. excitation energy for $Ru(phen)_2(CN)_2$ solution at different $HClO_4$ concentrations. Curve numbering corresponds to data in (A). Relative yields between different acid concentrations are correct.

We next estimated the first acid association constant. We define an apparent first association constant K' by

$$K' = (1 - F_D)/F_D[H^+] \qquad (3)$$

K' decreased with increasing $[H^+]$ because of the presence of the second protonation reaction. Plots of $(K')^{-1}$ vs. $[H^+]$ were visually linear for $[H^+] \leq \sim 1$ M, and a linear least-squares fit was used to extrapolate $(K')^{-1}$ to $[H^+] = 0$ where the second protonation reaction was unimportant. This intercept yielded a K_1 of 1.36 M^{-1} for both $Ru(phen)_2(CN)_2$ and $Ru(bpy)_2(CN)_2$. Using this K_1, K_2 was then estimated by a least-squares technique as follows. F_D vs. $[H^+]$ was calculated for differing K_2's until the sums of the squares of the residuals between the observed and calculated F_D curves were minimized for $0 \leq [H^+] \leq 2$ M. The best fit K_2 was 0.85 M^{-1} for both complexes. The calculated distribution of the three species is shown in Figure 3. Estimated error bounds in K_1 and K_2 are ~0.3 and ~0.4 M^{-1}, respectively.

Using the above calculated compositions of the solutions, it was then possible to deconvolute the absorption spectra of HD^+ and H_2D^{2+} from the experimental data. At low $[H^+]$ the solution was predominantly D and HD^+, and at high $[H^+]$ mainly HD^+ and HD^{2+} were present. The spectra for one low- and one high-acidity solution were used for the initial fit (e.g., 0.24 and 1.92 M for $Ru(phen)_2(CN)_2$). A zeroth-order spectrum of HD^+ was calculated assuming that the absorbance of the low-acidity solution arose from only D and HD^+. Using

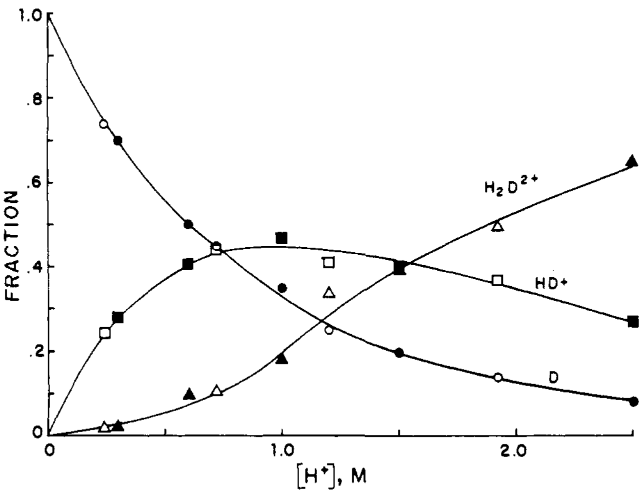

Figure 3. Fractional composition of $RuL_2(CN)_2$ solutions at different acid concentration. Filled symbols are for $Ru(phen)_2(CN)_2$ and open symbols are for $Ru(bpy)_2(CN)_2$. Circles are the measured fraction of free D. Squares are the calculated HD^+ values, and triangles are the calculated H_2D^{2+} points. The solid lines are smooth curves drawn through the data, but are not calculated.

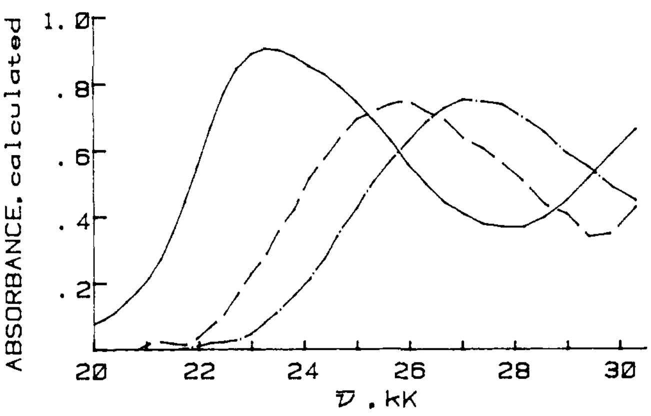

Figure 4. Spectra for $Ru(bpy)_2(CN)_2$ (—), $[Ru(bpy)_2(CN)(CNH)]^+$ (- - -), and $[Ru(bpy)_2(CNH)_2]^{2+}$ (- · · · -). Data are for a 7.7×10^{-6} M solution in a 10-cm path length cell and were derived from the data of ref 7.

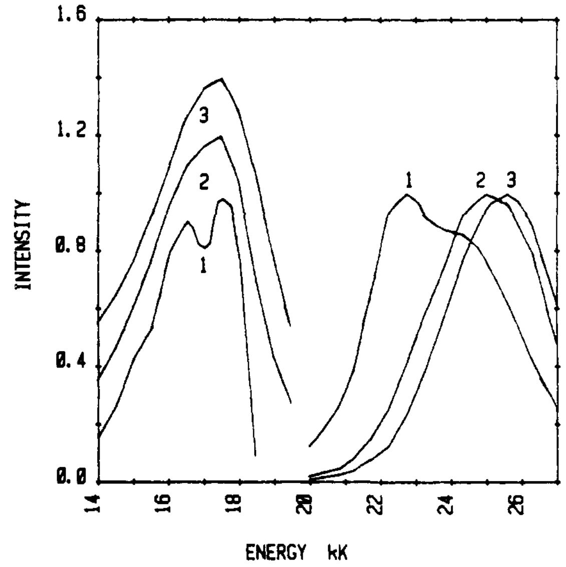

Figure 5. Low-temperature (77 K) emission spectra (left side) and corrected excitation spectra (right side) of $Ru(phen)_2(CN)_2$ in methanol-water (1), 1.2 M HCl in methanol-water (2), and 2.4 M HCl in methanol-water (3). Solutions were made up using 8 mL of methanol and diluting to a final volume of 10 mL with water and concentrated HCl to yield the indicated room temperature HCl concentrations. Emission spectra 2 and 3 are offset by 0.2 and 0.4 intensity units, respectively.

F_D from Figure 3 and the known absorption spectrum of D, the observed spectrum was corrected for the D component and the concentration of HD^+ to yield an approximation of the HD^+ spectrum. Then, using this approximate HD^+ spectrum, the H_2D^{2+} spectrum was obtained from the high-acidity absorbance curve by correcting for the D and HD^+ absorbance contributions. The low-acidity data were then corrected for the absorption contribution from H_2D^{2+} to obtain a new HD^+ spectrum. On repeating this process several times, rapid convergence to consistent HD^+ and H_2D^{2+} spectra was obtained. Figures 2B and 4 show the deconvoluted spectra of HD^+ and H_2D^{2+} along with the spectrum of D for both complexes. To verify the validity of this procedure, spectra at intermediate $[H^+]$'s calculated from the D, HD^+, and H_2D^{2+} spectra and the solution compositions were compared with the observed absorption spectra. The fits were within experimental error (typically better than ±0.02 absorbance unit difference out of a total absorbance of ~0.8).

77 K Results. In an attempt to obtain emission from the protonated forms, low-temperature emission spectra were run. We reasoned that, even if thermodynamically unstable, in the rigid glass the protonated forms might persist long enough to emit.

Figure 5 shows excitation and emission spectra for $Ru(bpy)_2(CN)_2$ methanol-water glasses at 77 K with no acid and 1.2 and 2.4 M in HCl. The decay times are 5.1 (0 MH^+), 5.9 (1.2 MH^+), and 6.9 μs (2.4 MH^+). Only minor perturbations on the normal yellow emission spectra of $Ru(bpy)_2(CN)_2$ result in spite of enormous spectral shifts in absorption (the solutions go from orange to colorless). Even in 12 M aqueous HCl at 77 K, the emission, while weaker, was still characteristic of the unprotonated form.

An even more acid medium, however, is concentrated sulfuric acid, particularly without added water.[16,17] The emission of $Ru(phen)_2(CN)_2$ in a concentrated (96%) H_2SO_4 glass at 77 K was found to be bright blue rather than the characteristic orange. This emission spectrum bears a striking resemblance to that of the $^3(\pi\text{-}^*\pi)$ phosphorescence of complexed phen (Figure 6). That this blue emission did not arise from free phen produced by decomposition of the complex was verified by attempts to excite the emission of a more concentrated phen solution in concentrated H_2SO_4. No emission at all was seen because of the long-wavelength cutoff of the Pyrex optical excitation system. Figures 6 and 7 show the emission spectra of $Ru(phen)_2(CN)_2$ and $Ru(bpy)_2(CN)_2$ in methanol-sulfuric acid glasses. The solvent composition is described in terms of the mole fraction (X) of H_2SO_4; the pure acid has $X = 0.83$ with the remainder being water. All of the H_2SO_4 glasses fractured badly and exhibited broad, featureless, short-lived emission blanks in the blue-UV region. All spectra are corrected for this emission blank, which never amounted to more than a few percent contribution to the total emission intensity. In the most acidic glasses used, we estimated that the relative quantum yield was at least a factor of 4 less than that of the unprotonated species. The media giving the structured blue emission gave no room temperature emission detectable above the rather strong solvent blank.

Decay times of the complexes in the H_2SO_4-methanol glasses are given in Figure 8. Ignoring the short-lived emission contribution from the H_2SO_4, the lifetimes at higher H_2SO_4 concentrations exhibited some nonexponentialities, but the deviations from exponentiality were not large enough to permit resolution into components.[18] Reported decay times represent the apparent τ obtained by linear least-squares fitting of the

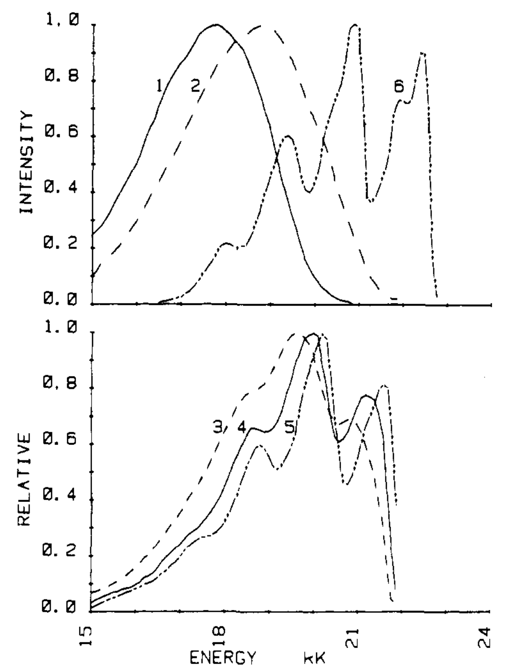

Figure 6. Low-temperature (77 K) emission spectra of $Ru(phen)_2(CN)_2$ in methanol-concentrated H_2SO_4 glasses. Pure methanol (1), $X = 0.09$ (2), 0.33 (3), 0.47 (4), and 0.83 (5). Curve 6 is corrected emission spectrum of the $^3(\pi\text{-}\pi^*)$ phosphorescence of $[Rh(phen)_3]^{3+}$ taken from ref 23.

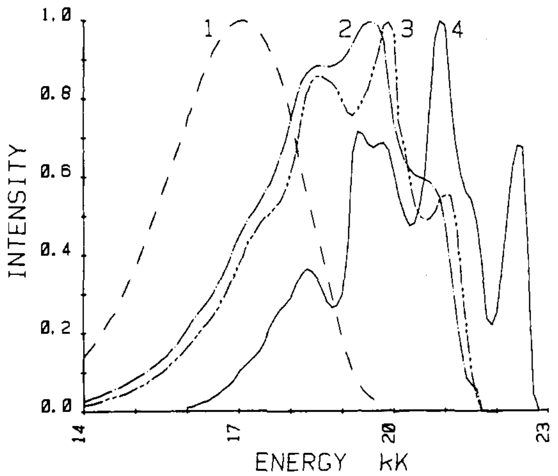

Figure 7. Low-temperature (77 K) emission spectra of $Ru(bpy)_2(CN)_2$ in methanol-concentrated H_2SO_4 glasses, $X = 0.07$ (1), 0.50 (2), and 0.83 (3). Curve 4 is the corrected $(\pi\text{-}\pi^*)$ phosphorescence of $[Rh(bpy)_3]^{3+}$ taken from ref 23. For clarity the spectrum in pure methanol was omitted, but this sample had two emission peaks at 17.3 and 16.15×10^3 cm^{-1} with relative intensities of 100:95.

logarithm of intensity vs. time plots after any short-lived contributions had died out; the fit was done over about 3 half-lives.

Discussion

Our results can be interpreted in the framework of the following excited-state acid–base reactions:

$$^*\mathrm{D} \xrightarrow{k_\mathrm{D}} \mathrm{D} + h\nu \text{ or heat} \tag{4}$$

$$^*\mathrm{D} + \mathrm{H}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^*\mathrm{HD}^+ \xrightarrow{k_\mathrm{HD}} \text{deactivated species} \tag{5}$$

$$^*\mathrm{HD}^+ + \mathrm{H}^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} {}^*\mathrm{H_2D}^{2+} \xrightarrow{k_\mathrm{H_2D}} \text{deactivated species} \tag{6}$$

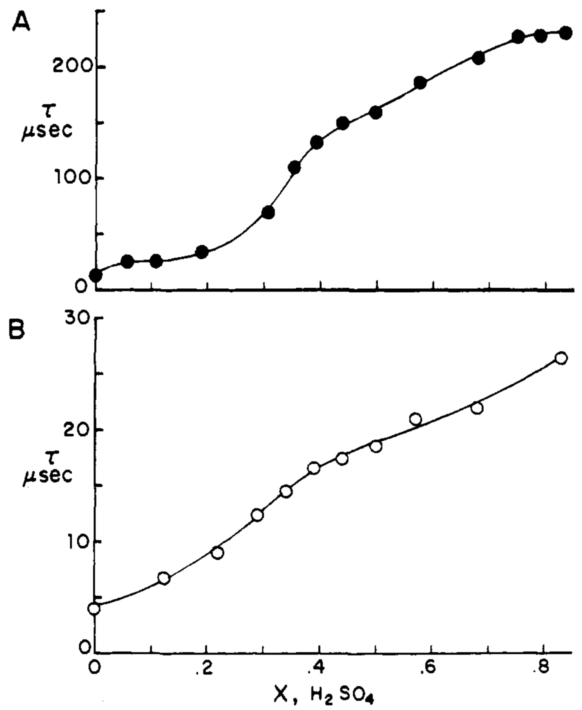

Figure 8. Lifetimes of $Ru(phen)_2(CN)_2$ (A) and $Ru(bpy)_2(CN)_2$ (B) in methanol-concentrated sulfuric acid glasses at 77 K vs. the mole fraction of H_2SO_4.

We begin by showing that at room temperature the interconversion of $^*H_2D^{2+}$ to $^*HD^+$ and $^*HD^+$ to $^*D$ proceeds without deactivation. Also, by far the dominant excited-state species is $^*D$ under the room temperature acidity conditions evaluated by us.

First, the low-energy absorption bands observed for HD^+ and H_2D^{2+} are clearly CT in nature. Their shape and intensities are very similar to that of the lowest energy CT band of the parent D species. These absorption bands are at too low an energy to arise from ligand-localized singlet states, and they are too intense ($\epsilon > 5000$) to arise from ligand field ($\epsilon < \sim 1000$) or spin-forbidden ligand absorptions. The emissions on exciting all the solutions, regardless of $[H^+]$, were always the same in energy and band shape as that of the unprotonated D, and the τ's in fluid solution were comparable to that of acid-free D. These characteristics show the fluid solution emissions to arise from a CT state. Given the enormous blue shift of the lowest energy observed CT bands of HD^+ and H_2D^{2+} relative to D ($\sim$2 and 3×10^3 cm^{-1}, respectively), it is inconceivable that the HD^+ and H_2D^{2+} emissions could be accidentally coincident in energy and band shape with the CT emission of D. Therefore, all the observed fluid solution emission must arise from $^*D$.

The invariance of the relative luminescence quantum yield with excitation wavelength for the different acid concentrations demonstrates unambiguously that interconversion of $^*H_2D$ to $^*HD^+$ to $^*D$ proceeds without deactivation. Consider, for example, the 0.72 M $[H^+]$-$Ru(phen)_2(CN)_2$ system. Figure 3 showed this solution to be ~45% D, ~45% HD^+, and 10% H_2D^{2+}. Yet excitation at 20.5×10^3 cm^{-1} where the sole absorbing species is D produced the same luminescence quantum yield (±5%) as when excitation was at 29.5×10^3 cm^{-1} where only ~20% of the available excitation energy was absorbed directly by D. Thus, $^*HD^+$ must convert to $^*D$ without deactivation. Similarly, at 1.92 M $[H^+]$, the ground-state composition was 10% D, 40% HD^+, and 50% H_2D^{2+}, yet the luminescence yield from D was the same regardless of whether the exciting light went essentially 100% into D (21.5×10^3 cm^{-1}) or ~55% into H_2D^{2+}, ~40% into HD^+, and ~5% into D. Thus,

$*H_2D^{2+}$ can convert without excited-state losses to *D. The most reasonable relaxation mode was $*H_2D^{2+} \rightarrow *HD^+ \rightarrow *D$ rather than a concerted loss of two protons ($*H_2D^{2+} \rightarrow *D$). Similar arguments on the $Ru(bpy)_2(CN)_2$ data demonstrate the same efficient excited state loss of protons as for the phen complex.[19]

We can estimate the room temperature excited-state equilibrium constants K_1*'s and K_2*'s by using the K_1's and K_2's and a Förster cycle.[1] The energy differences between the estimated absorption maxima of the principal CT bands of D, HD^+, and H_2D^{2+} were used as the energies spacing between the zero-point energies of their excited states. We obtain $K_1^* \sim 10^5$ M and $K_2^* \sim 10^2$ M for $Ru(bpy)_2(CN)_2$ and $K_1^* \sim 10^6$ M and $K_2^* \sim 10^2$ M for $Ru(phen)_2(CN)_2$. While these calculations should be considered as only guides, they indicate that $*H_2D^{2+}$ and $*HD^+$ are probably enormously more acidic than their ground-state counterparts. If these estimates are correct, then, even at the highest $[H^+]$ in our room temperature quenching measurements, $[*D] \gg [*HD^+] \gg [*H_2D^{2+}]$. This leads to $k_{-1} \gg K_{HD}$, $k_{-2} \gg k_{H_2D}$, $k_{-1} \gg k_1$, and $k_{-2} \gg k_2$. It is significant that, based on these pK*'s and room temperature H_0's of concentrated H_2SO_4,[16] significant equilibrium concentrations of $*HD^+$ or $*H_2D^{2+}$ could exist in these media. The failure to see emission from these media at room temperature probably arises from their long intrinsic lifetimes (vide infra) and thus high susceptibility to quenching by environmental factors. The decrease of emission intensity from D with increasing $[H^+]$ (Figure 2) appears to reflect the presence of small amounts of $*HD^+$ and $*H_2D^{2+}$ which are very efficiently quenched under the room temperature conditions. An excited-state equilibrium between the three forms ensures that interconversion between *D, $*HD^+$, and $*H_2D$ occurs without excited-state deactivation. A true excited-state equilibrium may not exist, however (see below), and our experimental results discussed above guarantee only that the interconversion of $*H_2D^{2+}$ to $*HD^+$ to *D proceeds without deactivation.

A comparison of the intensity quenching $[(\phi_0/\phi - 1)]$ and decay time quenching $[(\tau_0/\tau - 1)]$ vs. $[H^+]$ in aqueous $HClO_4$ shows interesting features. For both $Ru(bpy)_2(CN)_2$ and $Ru(phen)_2(CN)_2$, the plots do not appear to rise quite as rapidly as the ϕ plots. The discrepancies at up to 2 M may well be within our experimental error.[20] At high concentrations, however, the ϕ plots definitely rise more rapidly than the τ ones. At 3 M, for example, $\phi_0/\phi - 1 \sim 5$ while $\tau_0/\tau - 1 \sim 3.8$ for $Ru(phen)_2(CN)_2$; for $Ru(bpy)_2(CN)_2$ the corresponding values are ~2.0 and ~1.3. Maintenance of an excited-state equilibrium requires that $\phi_0/\phi - 1 = \tau_0/\tau - 1$ for all $[H^+]$ so long as all rate constants remain unchanged. The state energies of these polar cyano complexes are, however, quite solvatochromic. We suggest, therefore, that for $[H^+] > 2$ M the structure of the media may be changing radically enough to modify the rate constants for excited-state deactivations. Under these conditions equality between $\tau_0/\tau - 1$ and $\phi_0/\phi - 1$ need not be maintained.

The low-temperature results with $Ru(bpy)_2(CN)_2$ in HCl demonstrate additional features. The excitation spectra clearly show that even at 77 K much of the $Ru(bpy)_2(CN)_2$ exists as HD^+ and H_2D^{2+}; the equilibrium constants are not shifted with temperature in such a way as to make D the dominant ground-state species. Yet, even in 2.4 M HCl, the emission seems clearly to arise from $*Ru(bpy)_2(CN)_2$. The band energies and shapes as well as the τ's of the 2.4, 1.2, and 0 M HCl solutions are very similar. Thus, even at 77 K in this media, $*H_2D^{2+}$ and $*HD^+$ relax to *D before emission. That the observed emission is arising from an excitation of H_2D^{2+} and/or HD^+ is clearly demonstrated by the failure of the excitation spectra to match that of D while following that of HD^+ and/or H_2D^{2+}.

There are slight differences in the emission spectra of the different acidity HCl glasses. This result could be just a solvent effect. We favor an alternative interpretation. The absorption and emission of $Ru(bpy)_2(CN)_2$ are solvent dependent because of the large dipole-moment changes on going from the ground to the excited state. The solvent environment of HD^+ and H_2D^{2+} in the rigid glass will be slightly different than that of D because of the different ground-state dipole moments. On excitation, D, HD^+, and H_2D^{2+} all relax to *D, but in the rigid glass the environment around the resultant D will differ slightly depending on its source. Thus, D derived from D, HD^+, and H_2D^{2+} should have somewhat different emission spectra because of the differing microenvironments. This seems supported by the slight variations in emission spectra. The essential invariance of τ with $[H^+]$ would seem to rule out a simple solvent polarity effect.

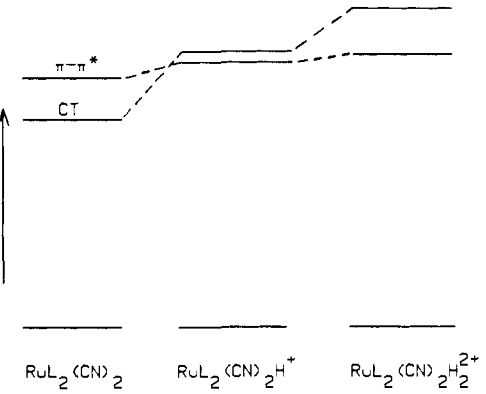

Figure 9. Schematic energy level diagram for relative positions of the lowest CT and $^3(\pi-\pi^*)$ states for $RuL_2(CN)_2$, $[RuL_2(CN)(CNH)]^+$, and $[RuL_2(CNH)_2]^{2+}$.

The 77 K measurements in H_2SO_4 present still a different picture. With increasing mole fraction of H_2SO_4, the emissions undergo dramatic blue shifts, spectral sharpening, and a remarkable enhancement of the τ's (for $Ru(phen)_2(CN)_2$ a factor of ~25 vs. a nonacidic glass). The sharpening and lifetime enhancement suggest more than just a simple increase in the energy of a CT emitting state on going from D to HD^+ to H_2D^{2+}.[21]

For comparison the emission spectra of the ligand localized $^3(\pi-\pi^*)$ phosphorescence of bound phen and bpy in RhL_3^{3+} are included in Figures 6 and 7. The RhL_3^{3+} emission spectra are corrected and a comparison of relative emission intensities of our data with these at widely different wavelengths is not possible. It is clear, however, that at the highest acid concentrations the emissions from the protonated $RuL_2(CN)_2$ complexes bear striking resemblances to those of the $^3(\pi-\pi^*)$ phosphorescences of the analogous RhL_3^{3+} species. Except for a lowering in energies of the emission maxima, the structure, energy spacing, and relative intensities of adjacent peaks are almost identical between the two series of complexes. For $Ru(phen)_2(CN)_2$ and $Ru(bpy)_2(CN)_2$ the lowerings in energy of the first emission maximum relative to RhL_3^{3+} are 0.9 and 0.5×10^3 cm^{-1}, respectively. We believe that the most reasonable interpretation of the emission changes in the $RuL_2(CN)_2$ complexes in the strongly acid H_2SO_4 media is that the normally lowest lying CT emitting state has been raised to such a high energy that it begins to mix strongly with or actually is at a higher energy than the lowest ligand localized $^3(\pi-\pi^*)$ state. This situation is shown diagrammatically in Figure 9.

In *D the CT emitting state is so much lower in energy than the lowest ligand $^3(\pi-\pi^*)$ state that, from a luminescence standpoint, the *D emission is essentially pure CT in nature. For $*HD^+$ we estimate the zeroth-order CT and $^3(\pi-\pi^*)$ to be very close in energy. This would result in strong mixing of the zeroth-order CT and $^3(\pi-\pi^*)$ states with a result that the emission of HD^+ is derived from a mixed state bearing considerable CT and $^3(\pi-\pi^*)$ character. For $^*H_2D^{2+}$ we estimate the zeroth-order CT state to be above the lowest $^3(\pi-\pi^*)$ level, which results in the emission being predominantly $^3(\pi-\pi^*)$ in character.

While the energy spacings of the states of Figure 9 cannot be assigned in detail, the gross features are supported by the data. Arguments are based principally on $Ru(phen)_2(CN)_2$, where the data are most persuasive, but the striking similarity between the emission data for $Ru(phen)_2(CN)_2$ and $Ru(bpy)_2(CN)_2$ implies that a similar interpretation holds for both complexes. First, the increased τ's and decreased quantum yields on going from D^+ to HD^+ to H_2D^{2+} demonstrate clearly that the intrinsic lifetime (τ_0's) of the emitting state is increasing even more than the observed τ's. We estimate that the τ_0 must be at least 1 ms for $^*[Ru(phen)(CNH)_2]^{2+}$. Such large τ_0's are substantially too long for CT emissions, especially when one considers that, except for the excited-state energies, the lowest CT absorptions of D, HD^+, and H_2D^{2+} are similar in intensities. τ_0's of ≥ 1 ms are, however, consistent with a state derived predominantly from one with $^3(\pi-\pi^*)$ character.

The failure of the emission spectra of the most acidic solutions to match that of the $^3(\pi-\pi^*)$ phosphorescence of the analogous $RnL_3{}^{3+}$ complexes bears comment. First, the ligand is bound to a different metal ion and has a different microenvironment; the $RhL_3{}^{3+}$ complexes have no dipole moment while the cyanide species have large permanent dipole moments. Either of these factors could account for the discrepancies, especially since the main $(\pi-\pi^*)$ singlet absorptions of $RuL_2(CN)_2$ complexes exhibit solvatochromism. An alternative explanation, however, may arise from the nearness of the $^3(\pi-\pi^*)$ and CT state to each other. The zeroth-order CT and $^3(\pi-\pi^*)$ states can mix and in doing so these resultant combination states will split away from the zeroth-order state energies. If the zeroth-order $^3(\pi-\pi^*)$ state were lowest, this splitting would force the predominantly $^3(\pi-\pi^*)$ state to energy lower than the zeroth-order state and correspondingly force the predominantly CT state to higher energy. Thus, although the emitting state would be predominantly $^3(\pi-\pi^*)$ in character, its energy would be below that of the zeroth-order $^3(\pi-\pi^*)$ state of the ligand.

We turn now to the approximate composition of the mixed emitting state of H_2D^{2+}. Assuming only mixing of the lowest $^3(\pi-\pi^*)$ and CT states, the intrinsic lifetime, τ_0, for a mixed state is given by

$$\tau_0 = \frac{1}{f_{CT}\tau_0{}^{-1}(\mathrm{CT}) + f_\pi\tau_0{}^{-1}(\pi)} \tag{7}$$

where f_x's are the fractions of each zeroth-order state in the actual mixed state wave function and $\tau_0(x)$'s are the intrinsic lifetimes if emission were only from the zeroth-order state. The "CT" and "π" scripting refers to the CT and $^3(\pi-\pi^*)$ zeroth-order states, respectively. Because we do not have quantum yields we are forced to use observed τ's rather than τ_0's; however, because the yields for the protonated forms are less than for *D, our calculations will overestimate f_{CT}. We begin by assuming that $\tau_0{}^{-1}(\pi) \ll \tau_0{}^{-1}(\mathrm{CT})$, which again overestimates f_{CT}. The estimation of $\tau_0{}^{-1}(\mathrm{CT})$ poses some problem. It is reasonable to assume, however, that $\tau_0(\mathrm{CT})$ is comparable to τ_0 for the unprotonated D because of the similar shape and intensity of the CT absorption spectra of D and H_2D. We use the observed lifetime for *D as $\tau_0(\mathrm{CT})$ and the observed lifetime of H_2D^{2+} for τ_0. Because of the lower luminescence yield of H_2D relative to D, this procedure overestimates f_{CT}. These assumptions yield f_{CT} for $[Ru(phen)_2(CN)_2]^{2+}$ of <5%, which bears out early suppositions that the emitting state of $[Ru(phen)_2(CNH)_2]^{2+}$ and possibly of $[Ru(bpy)_2(CNH)_2]^{2+}$ can be treated as predominantly $^3(\pi-\pi^*)$ states.

We will not make definitive statements concerning the emitting state of HD^+. We have no clear-cut range of $[H^+]$ where we can definitely say that the emission spectra arise from $^*HD^+$ and $^*H_2D^{2+}$. It seems likely, however, based on the steady increase in τ and decreasing yield with increasing $[H_2SO_4]$, that the emitting state is acquiring a steadily increasing contribution of $^3(\pi-\pi^*)$ character.[22]

The data for $Ru(bpy)_2(CN)_2$ vs. $Ru(phen)_2(CN)_2$ (Figure 8) suggest that the excited-state protonation of $Ru(bpy)_2(CN)_2$ is not so advanced as for the phen complex; indeed, it appears possible that only minor amounts of the $^*H_2D^{2+}$ may be present for $Ru(bpy)_2(CN)_2$. If so, the pK^* for $Ru(bpy)_2(CN)_2$ is more negative than that of the phen complex. Based on the shifts in the absorption spectra of these complexes on protonation and using the Förster equation,[1] we estimate the pK^* of $Ru(bpy)_2(CN)_2$ to be ~1 pK unit more negative than that of $Ru(phen)_2(CN)_2$, which is consistent with our τ data.

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References and Notes

(1) C. A. Parker, "Photoluminescence of Solutions", American Elsevier, New York, 1968.

(2) (a) W. Klöffer, *Adv. Photochem.*, **10**, 311 (1977); (b) S. G. Schulman, "Modern Fluorescence Spectroscopy", Vol. 2, Plenum Press, New York, 1976, p 239.

(3) (a) M. K. DeArmond, *Acc. Chem. Res.*, **7**, 309 (1974); (b) G. A. Crosby, *ibid.*, **8**, 231 (1975).

(4) (a) R. J. Watts and G. A. Crosby, *J. Am. Chem. Soc.*, **93**, 3184 (1971); (b) R. J. Watts, T. P. White, and B. G. Griffith, *ibid.*, **97**, 6914 (1975); (c) R. J. Watts, J. S. Harrington, and J. VanHouten, *ibid.*, **99**, 2179 (1977); (d) R. Ballardini, G. Varani, L. Moggi, V. Balzani, K. R. Olson, F. Scandolo, and M. Z. Hoffman, *ibid.*, **97**, 728 (1975); (e) B. Ballardini, G. Varani, L. Moggi, and V. Balzani, *ibid.*, **99**, 6881 (1977); (f) R. J. Watts and J. VanHouten, *ibid.*, **100**, 1718 (1978); (g) P. J. Giordano, S. M. Fredericks, M. S. Wrighton, and D. L. Morse, *ibid.*, **100**, 2257 (1978).

(5) (a) J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **93**, 1800 (1971); (b) F. Bolletta, M. Maestri, and V. Balzani, *J. Phys. Chem.*, **80**, 2499 (1976); (c) R. Bensasson, C. Salet, and V. Balzani, *J. Am. Chem. Soc.*, **98**, 3722 (1976); (d) J. N. Demas, E. W. Harris, and R. P. McBride, *ibid.*, **99**, 3547 (1977); (e) P. E. Hoggard and G. B. Porter, *ibid.*, **100**, 1457 (1978); (f) J. N. Demas, R. P. McBride, and E. W. Harris, *J. Phys. Chem.*, **80**, 2248 (1976); (g) N. A. P. Kane-Maguire, *Inorg. Chem.*, **15**, 464 (1976).

(6) (a) H. Gafney and A. W. Adamson, *J. Am. Chem. Soc.*, **94**, 8238 (1972); (b) C. R. Bock, T. J. Meyer, and D. G. Whitten, *ibid.*, **96**, 4710 (1974); (c) G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *ibid.*, **98**, 2337 (1976); (d) G. D. Jonak, M. S. Matheson, and D. Meisel, *ibid.*, **100**, 1449 (1978); (e) C-T. Lin, M. Chou, C. Creutz, and N. Sutin, *ibid.*, **98**, 2337 (1976); (f) C-T. Lin and N. Sutin, *ibid.*, **97**, 3543 (1975); (g) M. A. Hoselton, C-T. Lin, H. A. Schwarz, and N. Sutin, *ibid.*, **100**, 2383 (1978); (h) J. S. Winterle, D. S. Kliger, and G. S. Hammond, *ibid.*, **98**, 3719 (1976); (i) R. C. Young, J. K. Nagle, T. J. Meyer, and D. G. Whitten, *ibid.*, **100**, 4773 (1978); (j) B-T. Ahn and D. R. McMillin, *Inorg. Chem.*, **17**, 2253 (1978).

(7) S. H. Peterson and J. N. Demas, *J. Am. Chem. Soc.*, **98**, 7880 (1976).

(8) P. J. Giordano, C. R. Bock, M. S. Wrighton, L. V. Interrante, and R. F. X. Williams, *J. Am. Chem. Soc.*, **99**, 3187 (1977).

(9) M. Hunziker and A. Ludi, *J. Am. Chem. Soc.*, **99**, 7370 (1977).

(10) J. N. Demas, T. F. Turner, and G. A. Crosby, *Inorg. Chem.*, **8**, 674 (1969).

(11) J. N. Demas, M. G. Weiss, and D. Diemente, in preparation.

(12) D. G. Taylor, T. J. Turley, S. H. Peterson, M. L. Rodgers, and J. N. Demas, submitted.

(13) J. N. Demas and C. M. Flynn, Jr., *Anal. Chem.*, **48**, 353 (1976).

(14) J. N. Demas and J. W. Addington, *J. Am. Chem. Soc.*, **98**, 5800 (1976).

(15) (a) D. G. Taylor, M.S. Thesis, University of Virginia, 1976; (b) D. G. Taylor and J. N. Demas, *Anal. Chem.*, **51**, 712 (1979).

(16) (a) C. H. Rochester, "Acidity Functions", *Org. Chem. Ser. Monogr.* **17** (1970); (b) M. Liler, "Reaction Mechanisms in Sulfuric Acid", *ibid.*, **23** (1971).

(17) Judging by the Hammett acidity function, H_0, at room temperature, 12 M HCl is about five orders of magnitude less acidic than the 96 wt % sulfuric acid used in this study.[16]

(18) In the $Ru(phen)_2(CN)_2$ data, for example, the plateaus at 23, 160 and 230 μs suggested trying to fit the experimental data as a sum of exponentials with these three lifetimes. Fits of our data to a two-exponential expression with appropriate plateaus τ's, of course, resulted in improved fits. Numerical simulation of decay data with added noise, however, showed that the fitting parameters could be varied over a wide range without exceeding the probable error limits.

(19) It could be argued that the absence of emission from $^*HD^+$ and $^*H_2D^{2+}$ arises from efficient bimolecular quenching of these species by D. This possibility is ruled out by the low concentrations employed. Either the quenching constants required to produce our observed results would have to exceed 10^{12} M^{-1} s^{-1}, an impossibility, or the luminescence decay curves of $^*D$ would have to exhibit measurable rise times, which is not observed.

(20) $(\phi_0/\phi - 1) \sim 1.05$ and $\tau_0/\tau - 1 \sim 0.80$ for Ru(phen)$_2$(CN) at 1.5 M $HClO_4$ while the corresponding values are 0.27 and 0.18 at 1.5 M $HClO_4$ for Ru(bpy)$_2$(CN)$_2$.

(21) Alternative explanations of the appearance of the HD^+ and H_2D^{2+} emissions are (1) the media hinders equilibration of the excited state by decreasing k_{-1} and k_{-2} or (2) the media decreases the quenching component in k_{H_2D} and k_{HD}. We consider these possibilities unlikely. Only emission from D is seen in glasses composed of aqueous 12 M HCl or methanol-water HCl glasses even though only protonated species are excited. With the far stronger acid, H_2SO_4, emissions of protonated species are seen, however, in methanol-water-sulfuric acid mixtures over a wide range in sulfuric acid and methanol concentrations. These possibilities would require either an enormous ability of the sulfuric acid media to suppress thermodynamically allowed excited-state deprotonation or a remarkable selectivity in the low-temperature media for deactivating one species in preference to another. To us the equilibrium maintenance of detectable amounts of $^*HD^+$ and $^*H_2D^{2+}$ at 77 K by the high acidity of these media is much more reasonable.

(22) This statement is based on the assumption that the relative energies of the CT states are changing continuously relative to the $^3(\pi-^*\pi)$ even for a given species. This, in turn, causes large changes in the $^3(\pi-^*\pi)$ component of the emitting state (eq 7). In view of the large solvatochromic shifts of the excited states of the complexes, this assumption seems quite reasonable.

(23) D. W. H. Carstens, Ph.D. Thesis, University of New Mexico, 1969.

Preparation and Reactivity of Some η^2-S_2 and η^2-Se_2 Complexes of Osmium and the X-ray Crystal Structure of $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$

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Abstract: The compounds $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$, $Os(\eta^2\text{-}Se_2)(CO)(CNR)(PPh_3)_2$ where R = *p*-tolyl, and $Os(\eta^2\text{-}S_2)(CO)_2(PPh_3)_2$ have been prepared. The reactivity of the $(\eta^2\text{-}S_2)$ and $(\eta^2\text{-}Se_2)$ ligands has been investigated and, in contrast to that of the $(\eta^2\text{-}O_2)$ analogues, which are oxidizing in character, has been found to be reducing in nature. Thus the ligands are readily attacked by alkylating agents to give cations of the type $[Os(\eta^2\text{-}Se_2Me)(CO)_2(PPh_3)_2]^+$ which react further with borohydride to yield complexes of the type $Os(H)(\eta^1\text{-}Se_2Me)(CO)_2(PPh_3)_2$. Reaction with iodine or dinitrogen tetroxide yields the known complexes $OsI_2(CO)_2(PPh_3)_2$ and $Os(NO_3)_2(CO)_2(PPh_3)_2$, respectively, with elemental selenium or sulfur being liberated. Reactions involving electrophiles such as NO^+ and RN_2^+ have been observed in which nitric oxide and nitrogen are evolved with elemental sulfur or selenium being deposited, followed by subsequent decomposition of the osmium residue in the absence of suitable ligands. The structure of dicarbonylbis(triphenylphosphine)diseleniumosmium(0) has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the triclinic space group $P\bar{1}$, with two molecules in a cell of dimensions a = 10.479 (1) Å, b = 17.933 (3) Å, c = 10.416 (2) Å, α = 103.49 (3)°, β = 115.10 (1)°, and γ = 75.72 (2)°. Refinement by least-squares techniques, using 5319 observations above background, gave a final agreement factor on F of 0.034. The coordination geometry at the Os atom is that of a distorted octahedron, with trans phosphine ligands and the Se_2 ligand "sideways" bonded. The Se-Se distance is lengthened to 2.321 (1) Å upon coordination. ESCA spectra show that the S_2 and Se_2 ligands are very effective at removing electron density from the Os atom.

Experimental Section

Infrared data were recorded on a Beckman IR 12 spectrophotometer and ^1H NMR spectra were obtained on a Varian T-60 spectrometer. Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany. Melting points (uncorrected) were measured on a Reichert hot stage microscope. ESCA spectra were recorded using a McPherson ESCA 36 spectrometer and an Al anode. The carbon 1s peak of graphite was used as an internal reference (284.0 eV). Samples were smeared on graphite-coated Al plates.

Preparation of Starting Materials. A. $Os(CO)_2(PPh_3)_3$. $Os(H)ClCO(PPh_3)_3$[2a] (3.0 g) and $AgClO_4$ (0.596 g) were refluxed in CH_3CN (80 mL) for 1 h. The solution was cooled to 60 °C and filtered quickly using warmed glassware. Solvent was removed under reduced pressure and the residue was recrystallized from a mixture of CH_2Cl_2 and ethanol to yield 2.62 g (99%) of $[Os(H)CO(CH_3CN)_2(PPh_2)_2]^+ClO_4^-$.[2b]

This product (2.0 g) was heated at 50 °C in CH_2Cl_2 (60 mL) under an atmosphere of CO (40 psi) for 90 min. It was then filtered and ethanol (60 mL) added followed by 70% $HClO_4$ (0.5 mL). Evaporation to a volume of 30 mL gave white crystals, 1.96 g (99%), of $[Os(H)(CO)_2(CH_3CN)(PPh_3)_2]^+$ ClO_4^-.

This product (1.6 g) and PPh_3 (3.0 g) were heated under reflux in 2-methoxyethanol (200 mL) for 24 h. The solution was evaporated to dryness and extracted twice with hot hexane (100 mL) to remove excess phosphine. The remaining oily solid was dissolved in CH_3OH (100 mL) and filtered. Crushed NaOH (0.6 g) was added, and the system was flushed with nitrogen gas and then heated under reflux for 1 h.

The resulting yellow needles were filtered off and washed with ethanol and hexane, yield 1.27 g (70%), mp 164-166 °C. Anal. Calcd for $C_{56}H_{45}O_2OsP_3$: C, 65.73; H, 4.39; P, 9.00. Found: C, 65.16; H, 4.54; P, 8.39.

B. $Os(CO)(CNC_7H_7)(PPh_3)_3$.[3] $Os(H)ClCO(PPh_3)_3$[2a] (3.65 g) and C_7H_7NC (0.45 g) were heated under reflux in benzene (180 mL) for 10 min. The solution was then cooled and evaporated with continuous addition of ethanol (100 mL) until the final volume was 50 mL. Hexane (50 mL) was then added to ensure complete crystallization and the product filtered off and recrystallized from CH_2Cl_2 and ethanol to yield 3.14 g (100%) of $Os(H)ClCO(CNC_7H_7)(PPh_3)_2$.

This product (2.10 g) and $AgClO_4$ (0.495 g) were heated under reflux in a mixture of benzene (50 mL) and ethanol (20 mL) for 3 h. The solvent was removed under reduced pressure and the residue was dissolved in the minimum of CH_2Cl_2 and filtered. Ethanol (30 mL) was added and the solvent removed until a final volume of 15 mL was achieved when hexane (50 mL) was added. The solid was filtered off and washed with ice-cold ethanol and hexane. A yield of 2.15 g (96%) of $Os(H)ClO_4(CO)(CNC_7H_7)(PPh_3)_2$ was obtained.

This product (1.47 g) and PPh_3 (0.50 g) were heated under reflux

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