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 RuL3(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 H2D2+ can coexist with D, but on excitation *HD+ and *H2D2+ are such strong acids and they deprotonate so rapidly (*H2D2+ → HD+ → 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 H2SO4–methanol glasses, emission from the protonated forms occurs. With Ru(phen)3(CN)2 and possibly with Ru(bpy)3(CN)2, the lowest CT state of H2D2+ 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. In spite of the enormous recent interest in luminescent transition metal complexes, however, information on their excited-state acid–base properties is still quite limited. 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)3(CN)2, in aqueous acid. The two cyano groups are basic and under highly acidic conditions ([H+] ≥ ~0.2 M) solutions contain H2D2+, HD+, and D in equilibrium (D = RuL3(CN)2). Emission from these acidified aqueous solutions, however, shows only the emission spectrum of *D, regardless of the concentration of HClO4. Emission quenching by [H+] also shows non-Stern–Volmer behavior, but the luminescence quantum yields from *D are independent of whether H2D2+, 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 H2D2+ and D where D is [Ru(bpy)3]2(4,4'-HOOC)2(bpy)]2+.

We wish to report here additional studies on Ru(bpy)3(CN)2 and results for the similar dicyanobis(1,10-phenanthroline)ruthenium(II), Ru(phen)3(CN)2. These systems are unique in that 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)3(CN)210 and Ru(phen)3(CN)211 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 tri(hydroxymethy1)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 Emission was monitored with a 1-kW Phase-R pulsed nitrogen laser, or a Molectron UV-14 400-kW nitrogen laser. The excitation beam was passed through a 1-cm aqueous solution filter of CuSO4,5H2O (100 g/L). With the Molectron laser, the emission was isolated with a Jobin-Yvon H10 holographic grating monochromator. Emissions were observed with an RCA 6342 photomultiplier tube. To reduce scattered stray light a 1-cm solution filter of saturated aqueous NaN32O 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 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; 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 < 0.5). 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)3(CN)2 in water at different concentrations of HClO4 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 H2D2+ as is observed for Ru(bpy)3(CN)2 where similar absorption changes with [H+] are seen.13 Acidified solutions of Ru(phen)3(CN)2 and Ru(bpy)3(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, \(\theta(v)\), for the mixtures were calculated from excitation spectra by

\[
\theta(v) = \frac{O(v)}{G(v)[1 - \exp(-2.303A(v))]} \tag{1}
\]
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; G, 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 \( O(\overline{v}) \) is the observed intensity of emission of \( *D \) at excitation energy \( \overline{v} \) (observed at the emission maximum), \( I(\overline{v}) \) is the relative excitation source intensity obtained from the Rhodamine B quantum counter, and \( A_S \) 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 \( \theta(\overline{v}) \) an average value of unity across the normalization region for the acid-free solution.

Figure 2C shows the corrected relative luminescence quantum yield vs. \( \overline{v} \) 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. \( \overline{v} \) for Ru(bpy)\(_2\)(CN)\(_2\) have been reported elsewhere\(^2\) 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 HCIO4, either no emission was detectable or only the orange one was emitted. In 0.25 M HCIO4, however, attributed this decrease to photochemical decomposition of Ru(phen)\(_2\)(CN)\(_2\) at room temperature

To fully interpret the excitation spectra, the composition of the acidified solutions in terms of D, HD\(^+\), and H\(_2\)D\(^2+\) 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\(_2\)D\(^2+\) are transparent. This was shown by making plots of the fractional absorbance \( (F_D(\overline{v})) \) of the solutions relative to the unacidified solution.

\[
F_D(\overline{v}) = A_S([H^+]) / A_S(0)
\]

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

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

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

\( K' \) decreased with increasing [H\(^+\)] because of the presence of the second protonation reaction. Plots of \( (K')^{-1} \) vs. [H\(^+\)] were visually linear for [H\(^+\)] \( \leq 1 \text{ M} \), 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 \( 0 \leq [H^+] \leq 2 \text{ M} \). 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 \( \pm 0.3 \) and \( \pm 0.4 \text{ M}^{-1} \), respectively.

Using the above calculated compositions of the solutions, it was then possible to deconvolute the absorption spectra of HD\(^+\) and H\(_2\)D\(^2+\) from the experimental data. At low [H\(^+\)] the solution was predominantly D and HD\(^+\), and at high [H\(^+\)] mainly HD\(^+\) and H\(_2\)D\(^2+\) 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
the observed spectrum was corrected for the D component and the concentration of HD+ to yield an approximation of the contributions. The low-acidity data were then corrected for the absorbance curve by correcting for the D and HD+ absorbance the H2D2+ spectrum was obtained from the high-acidity absorption contribution from H2D2+ to obtain a new HD+ spectrum. Then, using this approximate HD+ spectrum, solutions in concentrated H2SO4. No emission at all was seen absorption spectra. The fits were within experimental error emit.

An attempt to excite the emission of a more concentrated phen to that of the \( \pi^* \) 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 H2SO4. 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 H2SO4; the pure acid has \( X = 0.83 \) with the remainder being water. All of the H2SO4 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 H2SO4-methanol glasses are given in Figure 8. Ignoring the short-lived emission contribution from the H2SO4, the lifetimes at higher H2SO4 concentrations exhibited some nonexponentialities, but the deviations from exponentiality were not large enough to permit resolution into components. Reported decay times represent the apparent \( \tau \) 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$_2$SO$_4$ 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 $^1(p-\pi^*)$ phosphorescence of [Rh(phen)$_2$]$^{3+}$ taken from ref 23.

Figure 7. Low-temperature (77 K) emission spectra of Ru(bpy)$_2$(CN)$_2$ in methanol-concentrated H$_2$SO$_4$ glasses, $X = 0.07$ (1), 0.50 (2), and 0.83 (3). Curve 4 is the corrected $(\pi-\pi^*)$ 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 $16.15 \times 10^3$ cm$^{-1}$ with relative intensities of 100:95.

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$_2$SO$_4$.

We begin by showing that at room temperature the interconversion of *H$_2$D$_2^+$ 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$_2$D$_2^+$ 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 ($\epsilon < ~1000$) 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 $\tau$'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$_2$D$_2^+$ relative to D ($\approx 2$ and $3 \times 10^3$ cm$^{-1}$, respectively), it is inconceivable that the HD$^+$ and H$_2$D$_2^+$ 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$_2$D 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 $\approx 45\%$ D, $\approx 45\%$ HD$^+$, and $\approx 10\%$ H$_2$D$_2^+$. Yet excitation at $20.5 \times 10^3$ cm$^{-1}$ where the sole absorbing species is D produced the same luminescence quantum yield ($\pm 5\%$) as when excitation was at $29.5 \times 10^3$ cm$^{-1}$ where only $\approx 20\%$ 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$_2$D$_2^+$, yet the luminescence yield from D was the same regardless of whether the exciting light went essentially 100% into D ($21.5 \times 10^3$ cm$^{-1}$) or $\approx 55\%$ into H$_2$D$_2^+$, $\approx 40\%$ into HD$^+$, and $\approx 5\%$ into D. Thus,

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

\[ *D \xrightarrow{k_2} D + h\nu \text{ or heat} \quad (4) \]

\[ *D + H^+ \xrightarrow{k_{1-1}} *HD^+ \xrightarrow{k_{HD}} \text{deactivated species} \quad (5) \]

\[ *HD^+ + H^+ \xrightarrow{k_{2-2}} *H_2D^+ \xrightarrow{k_{H_2D}} \text{deactivated species} \quad (6) \]
*H₂D²⁺ can convert without excited-state losses to *D. The most reasonable relaxation mode was *H₂D²⁺ → HD⁺ → *D rather than a concerted loss of two protons (*H₂D²⁺ → *D). Similar arguments on the Ru(bpy)₃(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 K₁, *s and K₂, *s by using the K₁, *s and K₂, *s and a Förster cycle.¹ The energy differences between the estimated absorption maxima of the principal CT bands of D, HD⁺, and H₂D²⁺ were used as the energies spacings between the zero-point energies of their excited states. We obtain K₁, * ~ 10⁵ M and K₂, * ~ 10³ M for Ru(bpy)₂(CN)₂ and K₁, * ~ 10⁶ M and K₂, * ~ 10² M for Ru(phen)₂(CN)₂. While these calculations should be considered as only guides, they indicate that *H₂D²⁺ 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 experiments, [*D] > [*HD⁺] > [*H₂D²⁺]. This leads to k₁ > K₁, *HD, k₂ > K₂, *H₂D, k₁ > k₁, and k₂ > k₂. It is significant that, based on these pK⁺,*s and room temperature pH₅.₀'s of concentrated H₂SO₄,¹⁶ significant equilibrium concentrations of *HD⁺ or *H₂D²⁺ could exist in these media. The failure to see emission from these media at room temperature suggests that the excited species are too unstable to emit. The decrease of emission intensity from D with temperature in such a way as to make D the dominant excited-state emitter is consistent with the presence of small amounts of *HD⁺ and *H₂D²⁺ 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 *H₂D 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 *H₂D²⁺ to *HD⁺ to *D proceeds without deactivation.

A comparison of the intensity quenching ([φ₀/φ - 1]) and decay time quenching ([τ₀/τ - 1]) vs. [H⁺] in aqueous HClO₄ 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, φ₀/φ ~ 1 ~ 5 while τ₀/τ ~ 1 ~ 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 φ₀/φ = 1 = τ₀/τ - 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 energy equality between τ₀/τ - 1 and φ₀/φ - 1 may 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 H₂D²⁺; 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, *H₂D²⁺ and *HD⁺ relax to *D before emission. That the observed emission is arising from an excitation of H₂D²⁺ 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 H₂D²⁺.

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 diol-moment changes on going from the ground to the excited state. The solvent environment of HD⁺ and H₂D²⁺ in the rigid glass will be slightly different than that of D because of the different ground-state diol moments. On excited state, HD⁺ and H₂D²⁺ 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 H₂D²⁺ 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.

The 77 K measurements in H₂SO₄ present still a different picture. With increasing mole fraction of H₂SO₄, 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 just a simple increase in the energy of a CT emitting state on going from D to HD⁺ to H₂D²⁺.²¹

For comparison the emission spectra of the ligand localized (π-π*) phosphorescence of bound phen and bpy in RhL₃³⁺ are included in Figures 6 and 7. The RhL₃³⁺ 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 RuL₂(CN)₂ complexes bear striking resemblances to those of the (π-π*) phosphorescences of the analogous RhL₃³⁺ 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)₃(CN)₂ and Ru(bpy)₃(CN)₂ the lowering in energy of the first emission maximum relative to RhL₃³⁺ are 0.9 and 0.5 × 10³ cm⁻¹, respectively. We believe that the most reasonable interpretation of the emission changes in the RuL₂(CN)₂ complexes in the strongly acid H₂SO₄ 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 (π-π*) 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 (π-π*) state that, from a luminescence standpoint, the *D emission is essentially pure CT in nature. For *HD⁺ we estimate the zeroth-order CT and (π-π*) to be very close in energy. This would result in strong mixing of

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Figure 9. Schematic energy level diagram for relative positions of the lowest CT and (π-π*) states for RuL₂(CN)₂, [RuL₂(CN)(CNH₃)₂]⁺, and [RuL₂(CNH₃)₂]²⁺.
the zeroth-order CT and $3(\pi-\pi^*)$ states with a result that the emitting state of $[\text{Ru}(\text{phen})_2(\text{CN})_2]^{2+}$ is 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 $\text{Ru}(\text{phen})_2(\text{CN})_2^2$, where the data are most persuasive, but the striking similarity between the emission data for $\text{Ru}(\text{phen})_2(\text{CN})_2$ and $\text{Ru}(\text{bpy})_2(\text{CN})_2$ implies that a similar interpretation holds for both complexes. First, the increased $\tau$'s and decreased quantum yields on going from D to $\text{H}_2\text{D}_2^2$ demonstrate clearly that the intrinsic lifetime ($\tau_0$) of the emitting state is increasing even more than the observed $\tau$'s. We estimate that the $\tau_0$ must be at least 1 ms for $[\text{Ru}(\text{phen})_{\text{CN}}]^{2+}$ of large $\tau_0$ is substantially too long for LT emissions, especially when one considers that, except for the excited-state energies, the lowest CT absorptions of D, $\text{H}_2\text{D}^*$, and $\text{H}_2\text{D}_2^2$ are similar in intensities. $\text{H}_2\text{D}_2^2$, in contrast, has a state derived predominantly from one with $3(\pi-\pi^*)$ character.

The failure of the emission spectra of the most acidic solutions to match of that of the $3(\pi-\pi^*)$ phosphorescence of the analogous $\text{RhL}_3^{2+}$ complexes bears comment. First, the ligand is bound to a different metal ion and has a different microenvironment; the $\text{RhL}_3^{2+}$ 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 $\text{RuL}_2(\text{CN})_2$ 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 $\text{H}_2\text{D}_2^2$. Assuming only mixing of the lowest $3(\pi-\pi^*)$ and CT states, the intrinsic lifetime, $\tau_0$, for a mixed state is given by

$$\tau_0 = \frac{1}{f_{CT} \tau_0^{-1}(CT) + f_3 \tau_0^{-1}(\pi)} \tag{7}$$

where $f_3$'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 "$\pi$" 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 $\tau$'s rather than $\tau_0$'s; however, because the yields for the protonated forms are less than for D, our calculations will underestimate $f_{CT}$. We begin by assuming that $\tau_0^{-1}(\pi) \ll \tau_0^{-1}(CT)$, which again overestimates $f_{CT}$. The estimation of $\tau_0^{-1}(\pi)$ poses some problem. It is reasonable to assume, however, that $\tau_0(\pi)$ is comparable to $\tau_0$ for the unprotonated D because of the similar shape and intensity of the CT absorption spectra of D and H2D. We use the observed lifetime for D as $\tau_0(\pi)$ and the observed lifetime of H2D2+ for $\tau_0$. Because of the lower luminescence yield of H2D2+ relative to D, this procedure overestimates $f_{CT}$. These assumptions yield $f_{CT}$ for $[\text{Ru}(\text{phen})_2(\text{CN})_2]^{2+}$ of <5%, which bears out early suppositions that the emitting state of $[\text{Ru}(\text{phen})_2(\text{CN})_2]^{2+}$ and possibly of $[\text{Ru}(\text{bpy})_2(\text{CN})_2]^{2+}$ can be treated as predominantly $3(\pi-\pi^*)$ states.

We will not make definitive statements concerning the emitting state of $\text{H}_2\text{D}^*$. We have no clear-cut range of $[\text{H}^+]$ where we can definitively say that the emission spectra arise from $\text{H}_2\text{D}^*$ and $\text{H}_2\text{D}_2^2$. It seems likely, however, based on the steady increase in $\tau$ and decreasing yield with increasing $[\text{H}_2\text{SO}_4]$, that the emitting state is acquiring a steadily increasing contribution of $3(\pi-\pi^*)$ character.22

The data for $\text{Ru}(\text{bpy})_2(\text{CN})_2^2$ vs. $\text{Ru}(\text{phen})_2(\text{CN})_2^2$ (Figure 8) suggest that the excited-state protonation of $\text{Ru}(\text{bpy})_2(\text{CN})_2^2$ is not so advanced as for the phen complex; indeed, it appears possible that only minor amounts of the $*\text{H}_2\text{D}^*$ may be present for $\text{Ru}(\text{bpy})_2(\text{CN})_2^2$. If so, the $pK^*$ for $\text{Ru}(\text{bpy})_2(\text{CN})_2$ 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 Forster equation, we estimate the $pK^*$ of $\text{Ru}(\text{bpy})_2(\text{CN})_2$ to be $\sim 1$ pK unit more negative than that of $\text{Ru}(\text{phen})_2(\text{CN})_2$, which is consistent with our $\tau$ data.

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References and Notes


Preparation and Reactivity of Some $\eta^2$-S$_2$ and $\eta^2$-Se$_2$
Complexes of Osmium and the X-ray Crystal Structure
of Os($\eta^2$-Se$_2$)(CO)$_2$(PPh$_3$)$_2$

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Abstract: The compounds Os($\eta^2$-Se$_2$)(CO)$_2$(PPh$_3$)$_2$, Os($\eta^2$-Se$_2$)(CO)(CN)(PPh$_3$)$_2$, where R = $p$-tolyl, and Os($\eta^2$-S$_2$)-(CO)$_2$(PPh$_3$)$_2$ have been prepared. The reactivity of the ($\eta^2$-S$_2$) and ($\eta^2$-Se$_2$) ligands has been investigated and, in contrast to that of the ($\eta^1$-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($\eta^2$-Se$_2$Me)(CO)(PPh$_3$)$_2$]$^+$ which react further with borohydride to yield complexes of the type Os(H($\eta^1$-Se$_2$Me)(CO)(PPh$_3$)$_2$) and Os(NO$_2$)(CO)(PPh$_3$)$_2$ respectively, with elemental selenium or sulfur being liberated. Reactions involving electrophiles such as NO$_2^+$ 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 dicarbonyl(bis(triphenylphosphine)diseleniuranium)(0) has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the triclinic space group P$ar{1}$, with two molecules in a cell of dimensions $a = 10.479$ (1), $b = 17.933$ (3), $c = 10.416$ (2), $\alpha = 103.49$ (3)$^\circ$, $\beta = 115.10$ (1)$^\circ$, and $\gamma = 75.72$ (2)$^\circ$. 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) $\AA$ 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 $^1$H NMR spectra were obtained on a Varian T-60 spectrometer. Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany. Melting points (un-corrected) were measured on a Reichert hot stage microscope. ESCA spectra were recorded using a McPherson ESCA 36 spectrometer and a Si anode. The carbon Is peak of graphite was used as an internal standard.

Preparation of Starting Materials. A. Os(CO)$_2$(PPh$_3$)$_2$. Os(H)-CICO(PPh$_3$)$_2$ (3.0 g) and AgClO$_4$ (0.596 g) were refluxed in CH$_2$CN (80 mL) for 1 h. The solution was cooled to 60 $^\circ$C and filtered quickly using warmed glassware. Solvent was removed under reduced pressure and the residue was recrystallized from a mixture of CH$_2$Cl$_2$ and ethanol to yield 2.62 g (99%) of [Os(H)(CO)(CH$_2$CN)(PPh$_3$)$_2$]*ClO$_4$.$^2$

This product (2.0 g) was heated at 50 $^\circ$C in CH$_2$Cl$_2$ (60 mL) under an atmosphere of CO (40 psi) for 90 min. It was then filtered and ethanol (50 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$_2$CN)(PPh$_3$)$_2$]*ClO$_4$.$^2$

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$_3$OH (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 $^\circ$C. Anal. Calcd for C$_{26}$H$_{22}$O$_2$P$_3$: C, 65.73; H, 4.39; P, 9.00. Found: C, 65.16; H, 4.19; P, 9.04.

B. Os(CO)(CN)$_2$(PPh$_3$)$_2$. Os(H)(CO)(CN)(PPh$_3$)$_2$ (3.65 g) and CH$_3$NC (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$_2$Cl$_2$ and ethanol to yield 3.14 g (100%) of Os(H)(CO)(CN)(CH$_3$NC)(PPh$_3$)$_2$ (3.65 g). 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$_2$Cl$_2$ 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)(CO)(CN)(CH$_3$NC)(PPh$_3$)$_2$ was obtained.

This product (1.47 g) and PPh$_3$ (0.50 g) were heated under reflux...