structural data reported. The two rhenium ions have octahedral coordination and are joined by three bridging chlorine atoms. Three carbonyl groups on each metal ion complete the coordination. The average Re–Cl distance is 2.51 Å while the average Re–C distance is 1.86 Å. The Re–Re distance is 3.37 Å, far too long to postulate any metal–metal bonding.

A brief note on the structure of the triiodide salt of the monocation octaethylporphinium species has appeared.[2] The porphyrin monocation in the present structure is in many ways very similar, even to the orientation of the terminal carbon atoms of the ethyl groups. In both compounds three rings are approximately coplanar, while the fourth is tilted with respect to the mean plane. In the present case the interplanar angles between the three approximately coplanar pyrrole rings from the mean plane of those rings range from 2.2 to 2.8°. The interplanar angle between this mean plane and the plane of the fourth ring (ring B) is 9.4°.

In the triiodide salt the pyrrolenine ring, which is the pyrrole ring not bearing a hydrogen atom was quite clearly indicated by a C–N–C angle of 102° as compared to angles of 109–110° in the other rings. In the present case the C–N–C angles in two adjacent rings (B and C) are 109.1 and 110.0°, while for the other two rings (A and D) the analogous angles are 106.5 and 104.3°. These two sets of angles are similar to those found in the neutral free bases[1] for pyrrole rings respectively bearing and lacking imino hydrogen atoms. It may be that one imino hydrogen atom position is disordered.

Within the relatively poor standard deviations, other bond lengths and angles in the pyrrole rings agree with those found for the free bases.[8] The distance between the pairs of diagonally situated nitrogen atoms is 4.11 Å for those in rings A and C and 4.06 Å for those in rings B and D.

There is a solvent molecule, most likely a water molecule, present. The oxygen atom is within hydrogen-bonding distance of three of the four pyrrole nitrogen atoms with N···O distances of 2.89–3.07 Å. The fourth N···O distance is 3.20 Å, probably too long to be considered a hydrogen bonding distance. There are no significant short intermolecular contacts between the anion and either the cation or the solvent molecule.

Further study is planned, including measuring a more extended data set to provide greater precision to positional and thermal parameters.

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Excited State Acid–Base Reactions of Transition Metal Complexes: Dicyanobis(2,2′-bipyridine)ruthenium(II) in Aqueous Acid

Sir:

We wish to report the first direct observation of an excited state acid–base reaction of a transition metal complex. Excited state acid-base reactions and equilibria in organic systems routinely have been directly observed by emission.[1] In inorganic systems, however, the presence of such reactions has only been inferred from the variation of photochemical yield with pH,[2] or in Cr(III) systems by OH^- quenching of the d-d luminescence,[3] but most results can be explained by reactions subsequent to the primary excited state process.

$Ru(bpy)_2(CN)_2$ (D) is a luminescent donor[4-6] of considerable interest. It exhibits a long-lived charge-transfer (CT) emission in fluid solution, and its neutrality frees it of the electrostatic repulsion and ion pairing problems of the widely used $[Ru(bpy)_3{}^{2+}]$.[7-12] In addition to being a good diffusional donor, D also possesses two CN's which can function as bridging ligands to transition metal ions and which gives rise to static association quenching; the first equilibrium constant can be evaluated from intensity and decay time data.[4,5] The two CN's are both sufficiently basic to be protonated.[13] While attempting to study the static and dynamic quenching of D by H^+, we discovered that $K_{sv}{}^{\tau}$ $(=(\tau_0/\tau - 1)/[H^+])$ was strongly dependent on $[H^+]$. $K_{sv}{}^{\tau} \approx 0.2\ M^{-1}$ at $[H^+] = 1$ M and 0.6 M^{-1} at $[H^+] = 4$ M. This unusual result suggested an excited state acid-base equilibrium, and we reexamined by spectrofluorimetry our original assumption that $[Ru(bpy)_2(CN)(CNH)]^+$ (HD^+) and $[Ru(bpy)_2(CNH)_2]^{2+}$ (H_2D^{2+}) were nonluminescent, instantly quenched species.

Figure 1 shows absorption spectra of D with varying concentrations of $HClO_4$. Up to $[H^+] \sim 0.6$ M, there is a near isosbestic point, and the solution consists predominantly of D and HD^+. At higher $[H^+]$, H_2D^{2+} is also present, and at $[H^+] = 2.5$ M, the mono- and diprotonated forms predominate. In luminescence, however, the sole emission is the broad featureless *D one (λ_{max} 635 nm) regardless of $[H^+]$ or λ_{exc} (350–450 nm). Thus, the only significant emission arises from *D.

To determine the sources of *D in the different solutions,

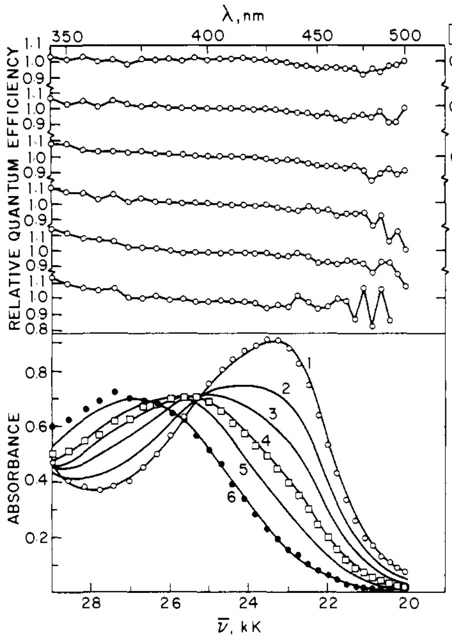

Figure 1. $Ru(bpy)_2(CN)_2$ spectra: Top, relative luminescence quantum yield in deoxygenated aqueous acid at ~21 °C. Each curve is normalized to unity, and yields at different acid concentrations cannot be compared. Bottom, absorption spectra (—) for acid concentrations of 0 M (1), 0.3 M (2), 0.6 M (3), 1.0 M (4), 1.5 M (5), and 2.5 M (6). Corrected excitation spectra at 0 M (○), 1 M (□), and 2.5 M (●). Absorbance measured in a 10-cm cell with 7.7×10^{-6} total donor concentration.

we measured the relative quantum yield of the *D emission vs. excitation energy $\bar{\nu}$:

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

where $O(\bar{\nu})$ is the observed luminescence intensity of *D, $I(\bar{\nu})$ is the corrected excitation intensity determined with a rhodamine B quantum counter (5 g/l. in methanol),[14] $A(\bar{\nu})$ is the *total* solution absorbance in the 1-cm spectrofluorimeter cell (<0.1), and thus $\theta(\bar{\nu})$ is the efficiency of *D emission on excitations of the mixture. G is a scale factor chosen to give each curve an average value of unity.[15]

Figure 1 shows that for $0 \leq [H^+] \leq 2.5$ M, $\theta(\bar{\nu})$ is independent of excitation wavelength within our experimental error. The slight decrease in $\theta(\bar{\nu})$ of acidic samples with decreasing $\bar{\nu}$ is in the same direction as the excitation scan, and we attribute it to photodecomposition. We estimate the following solution compositions: 0 M H^+–100% D; 0.6 M H^+–50% D, 40% HD^+, 10% H_2D^{2+}; 2.5 M H^+–8% D, 27% HD^+, 65% H_2D^{2+}. Thus, regardless of whether D, HD^+, or H_2D^{2+} is excited in a given solution, *D is produced with constant efficiency. The following model explains our results:

$$*D \xrightarrow{k_D} D + h\nu \text{ or heat} \qquad (2)$$

$$*D + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} *HD^+ \xrightarrow{k_{HD}} \text{deactivated species} \qquad (3)$$

$$*HD^+ + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} *H_2D^{2+} \xrightarrow{k_{H_2D}} \text{deactivated species} \qquad (4)$$

where k_D, k_{HD}, and k_{H_2D} are the sum of the first-order or $[H^+]$ independent pseudo-first-order processes deactivating *D, $*HD^+$, and $*H_2D^{2+}$, respectively. The $\theta(\bar{\nu})$ data show that both excited state deprotonation reactions proceed with 100% efficiency; consequently, $k_{-2} \gg k_{H_2D}$ and $k_{-1} \gg k_{HD}$.

Further, since the absolute luminescence quantum yields and τ's of *D in the mixtures decrease with increasing $[H^+]$,[16] the back reaction(s) must be important. Since direct deactivation of a CT excited state by H^+ has never been observed, we discount the reaction $*D + H^+ \rightarrow$ deactivated products. The most reasonable interpretation is that very small steady-state concentrations of $*HD^+$ and possibly $*H_2D^{2+}$ are generated with k_{HD} and possibly $k_{H_2D} \gg k_D$. In summary, our data seem consistent with an excited state equilibrium among *D, $*HD^+$, and $*H_2D^{2+}$ with the concentrations of the latter two being too low to detect directly by emission, but large enough that k_{HD} and k_{H_2D} can reduce the decay time and emission intensity of *D. The long lifetime of *D (100–260 ns) in these experiments should favor such an equilibrium situation. Further work is in progress.

Estimates of the first and second excited-state equilibrium constants by a Förster cycle also support our inability to see emission from $*HD^+$ or $*H_2D^{2+}$. We estimate $K_1 = 0.75 \pm 0.1$ M and $K_2 = 2 \pm 1$ M from ground state spectra and $K_1^* = 5 \times 10^5$ M and $K_2^* = 2 \times 10^8$ M using the principal CT absorption maximum of each of the three species to locate the relative zero-point energies of their excited states; the zero point energy of D is 1.85 μm^{-1},[5] and the absorption maxima for D, HD^+, and H_2D^{2+} are 2.32, 2.60, and 2.70 μm^{-1}, respectively.

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(15) Because $HClO_4$ solutions of D are somewhat thermally and photochemically unstable, especially at the higher $[H^+]$, absorption and excitation spectra were run concurrently on the same freshly prepared acidic samples. We do not yet know the nature of these reactions.
(16) A true excited state equilibrium with k_D independent of $[H^+]$ requires that $\theta/\theta_0 = \tau/\tau_0$. At high $[H^+]$ (>1.5 M), however, our preliminary data suggest that θ/θ_0 decreases somewhat more rapidly than τ/τ_0 (e.g., at $[H^+] = 1.5$ M, $\tau/\tau_0 = 0.62$ while $\theta/\theta_0 = 0.55$). It is currently unclear whether the θ results are due to an artifact in these measurements. Alternatively, an excited state equilibrium may not be established or k_D may be dependent on solution composition.

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Pseudorotation in Diphenyltrifluoroarsorane

Sir:

In two classical papers published in 1963–1964 Muetterties et al.[1,2] showed that fluorophosphoranes of the type R_2PF_3 were rigid at room temperature; i.e., they do not undergo Berry pseudorotation to any appreciable extent. Their ^{19}F NMR spectra consisted of a doublet of doublets and a doublet of triplets as a result of this rigidity. Much of the work and