by NSF Grant No. CHE-79-07027. We also thank Dr. Robert S. McDowell for experimental assistance. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, U.S. Department of Energy, under Contract Number DE-AC03-76SF00098.

Registry No. $Na_5[Gd(cat)_4]\cdot19.2H_2O$, 95531-51-4; $Na_6[Gd(cat)_3]_2\cdot20H_2O$, 95531-52-5; $Na[Gd(cat)_2]\cdot10H_2O$, 95531-53-6; $Na_6[Ho(cat)_3]_2\cdot20H_2O$, 95531-54-7; $Na_4[HF(cat)_4]\cdot21H_2O$, 69855-29-4.

Supplementary Material Available: Listings of shape parameters, anisotropic thermal parameters, hydrogen atom positions, and observed and calculated structure factors (Tables VII and XIII–XXI) for $Na_5[Gd(cat)_4]\cdot19.2H_2O$ and $Na_4[M(cat)_4]\cdot21H_2O$ (M = Hf, Ce, U, Th (72 pages). Ordering information is given on any current masthead page.

Notes

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Quenching of Photosubstitution in Ruthenium Polypyridine Complexes

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The photochemical behavior of ruthenium polypyridine complexes has become a topic of intense interest.[1] Extensive investigations of the photophysical properties of tris(bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, has led to the model shown in Figure 1.[2] In this model, the triplet metal-to-ligand charge-transfer state (^{3}MLCT) is populated with unit quantum efficiency. Once formed, the ^{3}MLCT undergoes three decay processes: radiative decay (k_r), radiationless decay (k_{nr}), and thermal population of a higher excited state ($k_0e^{-\Delta E/RT}$). This higher excited state has been identified as a ligand field state (LF) on the basis of the facts that it undergoes efficient radationless decay, is not luminescent, and results in a low-yield photosubstitution reaction.

Recently, the quenchings of both the luminescence and photosubstitution reaction have been investigated.[4] The specific system examined was $Ru(bpy)_3^{2+}$ in dimethylformamide (DMF) with 0.1 M tetrabutylammonium bromide present. The quencher selected was ferrocene. The resulting two linear Stern–Volmer plots were found to have substantially different slopes. In fact, the slope for the quenching of the photosubstitution was found to be 3-fold larger than the slope for the luminescence quenching. These results suggest that the ^{3}MLCT and LF states are not in thermal equilibrium. Furthermore, the lifetime of the LF states appears to be much longer than the ^{3}MLCT state.

These conclusions did not agree with some related results obtained in our laboratory so we decided to investigate the equivalent chloride system. The corresponding Stern–Volmer plots for the ferrocene quenching of both the luminescent lifetime and photosubstitution reaction of $Ru(bpy)_3Cl_2$ in DMF (0.1 M tetrabutylammonium chloride) are shown in Figure 2. The lifetime quenching plot yields a slope of 3070 ± 600 M^{-1}. The quenching rate constant is then evaluated as 4.0×10^9 L/(mol s), in good agreement with 5.9×10^9 L/(mol s) reported for the quenching in ethanol by Wrighton et al.[5] Evaluating the slope for quenching of the substitution process was much more difficult. The ferrocene absorbed a substantial fraction of the incident radiation, and itself undergoes a photoreaction.[4] Considering these difficulties, the difference in these two slopes (3070 ± 600 M^{-1} (τ_0/τ) vs. 1780 ± 700 M^{-1} (ϕ_0/ϕ)) is probably not significant, and in any case the trend is in contrast to the previous result in which the emission quenching had the smaller slope.

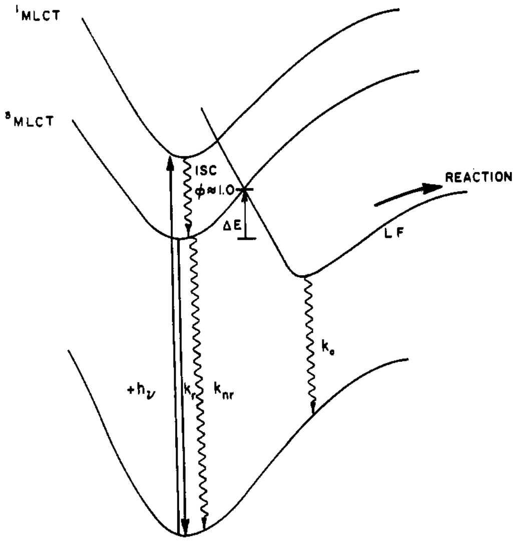

Figure 1. Photophysical processes of $Ru(bpy)_3^{2+}$.

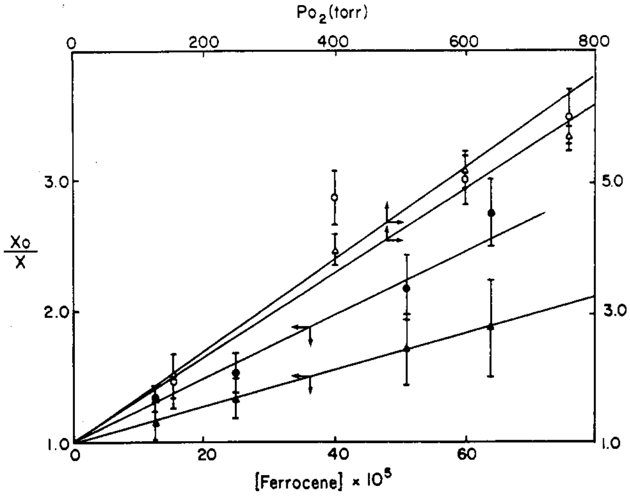

Figure 2. Stern-Volmer plots for the quenching of $Ru(bpy)_3^{2+}$ emission (triangles) and photosubstitution (circles) by ferrocene (solid) and oxygen (open). The progress of photosubstitution was monitored by the disappearance of $Ru(bpy)_3^{2+}$.

In order to avoid the problems associated with using ferrocene as a quencher, the quenchings of both the luminescence and photosubstitution by oxygen have been investigated. Oxygen is a good quencher but does not absorb any incident radiation. The same system ($Ru(bpy)_3^{2+}$ + Cl^-) in CH_3CN has been investigated.

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(1) The important references are too numerous to list here but the interested reader is referred to the following reviews: Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834. Seddon, K. R. *Coord. Chem. Rev.* **1982**, *41*, 79. Kalyanasundarau, K. *Coord. Chem. Rev.* **1982**, *41*, 159. Ford, P. C. *Rev. Chem. Intermed.* **1979**, *2*, 267. Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94. Balzani, V.; Boletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1. Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231.

(2) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 3843; **1976**, *98*, 4853. Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583. Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4803.

(3) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 3722. Bolleta, F.; Juris, A.; Maestri, M.; Sandrini, D. *Inorg. Chim. Acta* **1980**, *44*, L175.

(4) Fasano, R.; Hoggard, P. E. *Inorg. Chem.* **1983**, *22*, 566.

(5) Wrighton, M. S.; Pdungsap, L.; Morse, D. L. *J. Phys. Chem.* **1975**, *79*, 66.

As before, the Stern–Volmer plots for the quenching of both processes were determined and are displayed in Figure 2. The rate constant for luminescence quenching is evaluated as 6.8×10^8 L/(mol s),[6] somewhat lower than the values of 3.3×10^9 L/(mol s) (H_2O) and 1.7×10^9 L/(mol s) (MeOH) reported by Demas et al.[7] The quenching of the photosubstitution reaction was found to yield very nearly an identical Stern–Volmer plot (506 ± 40 M^{-1} (τ_0/τ) and 470 ± 60 M^{-1} (ϕ_0/ϕ)).

These results disagree with those previously reported and prompted us to reinvestigate the bromide system in DMF. Ferrocene was found to quench the ^{3}MLCT luminescence of $Ru(bpy)_3Br_2$ in DMF (0.1 M tetrabutylammonium bromide) at (nearly) a diffusion-controlled rate ($k_q = 3.2 \times 10^9$ L/(mol s)). The photosubstitution was also quenched. In fact, the linear Stern–Volmer plots had slopes that were identical within experimental error (1210 ± 200 M^{-1} (τ_0/τ) and 1170 ± 300 M^{-1} (ϕ_0/ϕ)). The value of these slopes agree reasonably well with the previously reported value for the luminescence quenching (826 ± 6 M^{-1})[4] but not with that for the quenching of photosubstitution (2530 ± 620 or 2825 ± 580 M^{-1}).[4] In order to further substantiate these conclusions, quenching by O_2 was attempted. Unfortunately, this proved to be unfeasible in DMF as explosions occurred at the higher O_2 pressures.

In order to avoid the dangers inherent with combustible solvents, the photosubsubstitution was examined in CH_2Cl_2 (0.01 M tetrabutylammonium bromide). Again, the quenchings of both the emission and photosubstitution by ferrocene were examined. The linear Stern–Volmer plots had similar slopes (4840 ± 500 M^{-1} (τ_0/τ) and 5070 ± 1200 (ϕ_0/ϕ)). The quenching by O_2 also resulted in liner Stern–Volmer plots with virtually identical slopes (166 ± 30 M^{-1} (τ_0/τ) and 147 ± 40 M^{-1} (ϕ_0/ϕ)).[6]

In conclusion, the quenchings of both the luminescence and photosubstitution are very similar. This indicates that the excited state affected by either ferrocene or O_2 is involved in both processes. Of course, the luminescence is known to occur from the ^{3}MLCT state. Quenching of this state also results in less population of the LF state and less photosubstituion. However, as long as only the ^{3}MLCT state is quenched by the additive, the ^{3}MLCT and LF need not be in thermal equilibrium to show similar Stern–Volmer plots.

Experimental Section

The quenching by ferrocene followed the procedure reported by Fasano and Hoggard.[4] The only exception was the use of phosphorescence lifetimes rather than intensities for evaluating the luminescence quenching. This avoids any inner-filter effects from the ferrocene.

For oxygen quenching, samples (3 mL) of solvent (0.1 M Cl^- or Br^-) were degassed and then equilibrated at the desired O_2 pressure. After equilibration for at least 1 h, the solution was drained into a cuvette that contained the appropriate amount of solid $Ru(bpy)_3Cl_2$ or $Ru(bpy)_3Br_2$. The sample was then sealed. *Care should be taken during the sealing process as there is a definite possibility of an explosion at the higher pressures of oxygen.* After sealing, the emission intensity and lifetime were evaluated. Finally, the photosubstituion quantum yield was determined by the method previously noted.

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Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; ferrocene, 102-54-5; oxygen, 7782-44-7.

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(6) The solubilities of O_2 in CH_2Cl_2 and CH_3CN were estimated with Henry's law. The coefficients for these solvents were approximated by a previously reported procedure. See: Osburn, J. O.; Markovic, P. L. *Chem. Eng.* **1969**, Aug, 105.

(7) Demas, J. N.; Diemente, D.; Harris, E. W. *J. Am. Chem. Soc.* **1973**, *95*, 6864.