increase in electron donation along the axial direction relieves the equatorial ligands somewhat, this being attested by the small decrease in $e_\sigma$(eq) value and the equally small increase in equatorial Cu-Cl bond length. Within the block of complexes B-D, a significant bridging role for two of the equatorial chlorine ligands is indicated by the AOM parameters. The increased bridging is associated geometrically with a greater proximity of the (still distant) axial ligands so that we see a continuing trend in smaller values for $e_\sigma$(eq) and decreasingly negative ones for $e_\sigma$(ax). The bridging chlorine atoms are each engaged—predominantly via $\sigma$ bonding—with two copper atoms and so will be less good donors—by both $\sigma$ and $\pi$ pathways—toward the reference copper atom. Some part of the decrease in the $e_\sigma$(eq) value on changing from E to B-D no doubt monitors this effect. The change in $\pi$ bonding is more clearly monitored by the AOM parameters. Finally, on moving to A, the geometric nature of the bridges changes and we observe the noncylindricality of the equatorial Cu-Cl interactions. The overall donation of charge from these ligands to the central metal has decreased a little—accompanied once again by an increased role for the axial ligands—as monitored by the smaller $e_\sigma$(eq) value (and marginally longer Cu-Cl bond) and by the fact that ($e_{\pi\parallel} + e_{\pi\perp}$) *may* be somewhat less here than for the complexes B-D.

Throughout these complex checks and balances—that accord with generally aquired chemical intuition—the sum $\Sigma$ of AOM parameters remains sensibly constant. In the Discussion we tried to present arguments that were not overdependent on the notion of the "sum rule", and to the extent that that was possible, therefore, the validity and utility of this transferability criterion is reasonably well demonstrated, at least, within the present series of chlorocuprate complexes. The concept is clearly one to be tested further in complexes involving other geometries, coordination numbers, and, of course, other metals and ligands.

**Registry No.** A, 18437-47-3; B, 16950-47-3; C, 55940-27-7; D, 55940-28-8; E, 95979-40-1; F, 51751-78-1; Cu, 7440-50-8; Cl, 7782-50-5.

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# Correlation of Ligand Field Excited-State Energies with Ligand Field Strength in (Polypyridine)ruthenium(II) Complexes

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*Received August 22, 1984*

The temperature dependence of the emission intensities and lifetimes for several (polypyridine)ruthenium(II) complexes have been evaluated. For complexes that have weaker ligand fields than tris(bipyridine)ruthenium(II), a dramatic decrease in the emission intensity and lifetime occurs near 170 K. This behavior is ascribed to population of a ligand field state that lies only 2000 cm$^{-1}$ above the lowest metal-to-ligand charge-transfer excited state. Above 250 K, a weak emission remains and an additional activated process can be observed in the vicinity of 260-330 K. This weak emission is assigned to emission from an impurity, most likely tris(bipyridine)ruthenium(II).

## Introduction

Extensive studies on tris(bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, have led to the model shown in Figure 1.[1] The intense absorption in the visible region (450 nm) has been assigned as a metal-to-ligand charge-transfer (MLCT) transition.[2] The initially produced $^1$MLCT rapidly undergoes intersystem crossing to the corresponding triplet state, $^3$MLCT, with unit efficiency.[3] This $^3$MLCT state is reasonably long-lived ($\approx$0.6 $\mu$s in water at 298 K) and is thought to be deactivated by three processes: radiative decay, $k_r$, radiationless decay, $k_{nr}$, and thermal population of a higher lying excited state, $k_0 \exp(-\Delta E/RT)$. For the latter process, Van Houten and Watts were able to evaluate the energy difference between these two states ($\Delta E$) as 3600 cm$^{-1}$ in water.[4] A low-yield photosubstitution occurs that is believed to result from population of this thermally accessable excited state.[5] As a result, the higher excited state has been designated a ligand field (LF) excited state.

However, the energy of this presumed LF state did *not* seem to depend upon the ligand field strength in the expected manner. For example, the 4,5-diazafluorene ligand (diaz) has been shown to selectively perturb LF states while leaving the energy of any MLCT states nearly unchanged.[6] However, for $Ru(bpy)_2diaz^{2+}$ over the temperature range of 250-350 K, the observed temperature dependence yielded a value of 3450 cm$^{-1}$ for $\Delta E$, very similar to that observed for $Ru(bpy)_3^{2+}$.[7] Another example is $Ru(bpy)_2(py)_2^{2+}$ (py = pyridine). Certainly pyridine is lower in the spectrochemical series than bipyridine, and the LF state is expected to occur at a lower energy. Again, the value of $\Delta E$ has been evaluated over the 250-350 K temperature range and found to be 3410 cm$^{-1}$.[8] Since the energy of the $^3$MLCT (relative to $Ru(bpy)_3^{2+}$ is essentially constant ($E_{em}$(0-0) varies by only 40 cm$^{-1}$), this value of $\Delta E$ suggests little change in the energy of the presumed LF state. Clearly, the ligand field trends so apparent in other metal complexes were absent in the behavior of this presumed LF state.

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[‡] Louisiana State University.

(1) The literature in this field is indeed rich with many more important contributions than can be listed, thus only a representative review is offered: 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. Balzani, V.; Boletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1. Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231. Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834.

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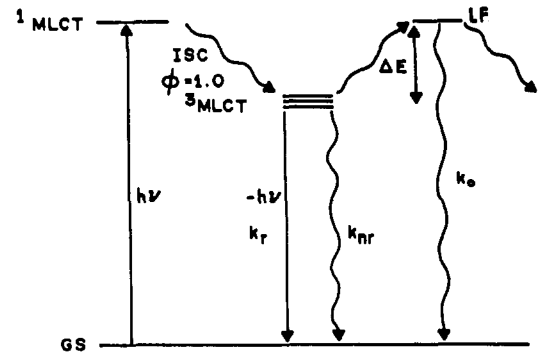

Figure 1. Photophysical properties of $Ru(bpy)_3^{2+}$.

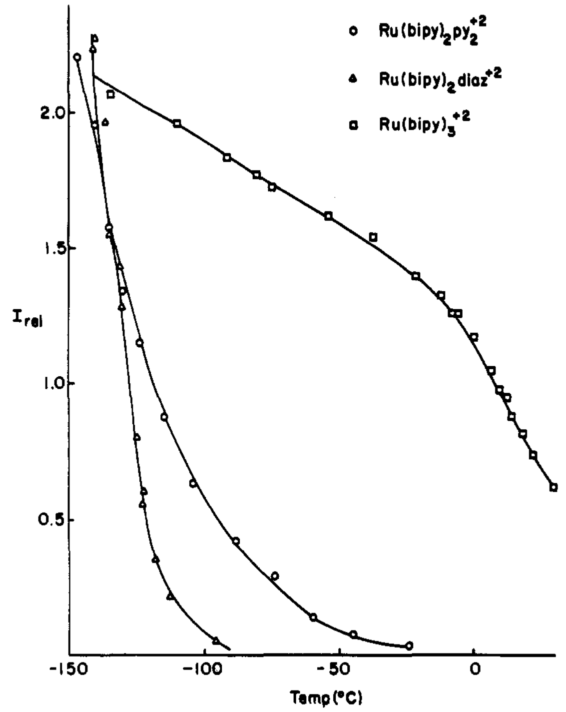

Figure 2. Emission intensity of $Ru(bpy)_3^{2+}$, $Ru(bpy)_2diaz^{2+}$, and $Ru(bpy)_2(py)_2^{2+}$ as a function of temperature. The solvent is EtOH/MeOH (4:1).

In order to further investigate changes in the energy of these LF states, the emission properties of $Ru(bpy)_2L^{2+}$ (L = diaz, $(py)_2$) complexes have been evaluated over an extended temperature range. For both complexes, a dramatic increase in the emission intensity and lifetime occur in the temperature range of 180–220 K. Furthermore, the emission previously reported at higher temperatures is suggested to arise from a small amount of $Ru(bpy)_3^{2+}$ impurity. Finally, the energy changes of the LF state can be adequately rationalized by ligand field theory.

## Results

The temperature dependence of the emission intensity for $Ru(bpy)_3^{2+}$, $Ru(bpy)_2diaz^{2+}$, and $Ru(bpy)_2(py)_2^{2+}$ are shown in Figure 2. The values for the lifetime displayed essentially the same behavior.

Previously, the emission intensity or lifetimes were fit to eq 1 by a nonlinear least-squares routine.[4,8] The resulting plots of $\phi^{-1}$

$$1/\phi = \frac{k_r + k_{nr} + k_0e^{-\Delta E/RT}}{k_r} \tag{1}$$

$$1/\tau = k_r + k_{nr} + k_0e^{-\Delta E/RT}$$

or $\tau^{-1}$ vs. $1/T$ for $Ru(bpy)_2diaz^{2+}$ in EtOH/MeOH (4:1) are shown in Figure 3. Clearly, eq 1 adequately describes the experimental data. Hence, no further exponential terms, as suggested by Allsopp et al.,[9] have been added to describe the very low-temperature region. Similar behavior was displayed by $Ru(bpy)_2L^{2+}$ (L = bpy, $(py)_2$).

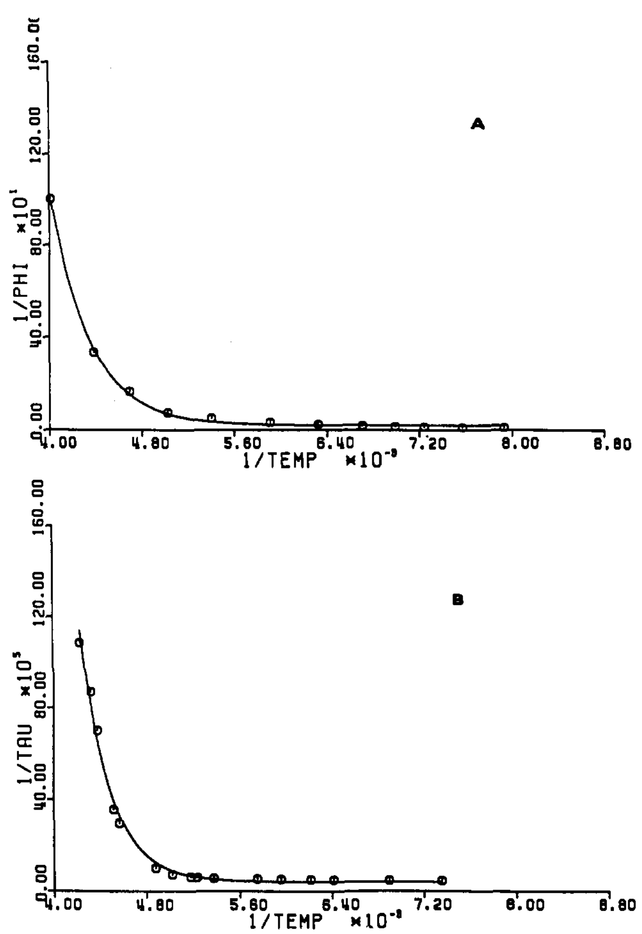

Figure 3. Comparison of experimental data with the computer-generated fit (eq 1) of the temperature dependence for the emission intensity (A) and lifetime (B) of $Ru(bpy)_3^{2+}$ in EtOH/MeOH (4:1).

The determination of $^3$MLCT production was also quantitated at 298 K by the method of Bolletta et al.[10] For $Ru(bpy)_3^{2+}$, the $^3$MLCT is quenched by $S_2O_8^{2-}$ via an electron-transfer mechanism. The resulting $S_2O_8^{3-}$ spontaneously dissociates so that electron transfer is effectively irreversible. The limiting quantum yield for $Ru(bpy)_3^{2+}$ dissappearance has been evaluated as 2,[9] a result we have substantiated. In contrast, $Ru(bpy)_2diaz^{2+}$ was virtually unchanged upon prolonged irradiation in the presence of $S_2O_8^{2-}$, and $Ru(bpy)_2(py)_2^{2+}$ underwent photoanation but not oxidation.

## Discussion

A dramatic change in the emission intensity and lifetime of $Ru(bpy)_2diaz^{2+}$ and $Ru(bpy)_2(py)_2^{2+}$ is apparent in the low-temperature region. At this point, it should be stressed that the solvent (EtOH/MeOH, 4:1) remains a liquid throughout this temperature region; the liquid–glass transition occurs at ≈95 K. For both complexes an additional activated process is apparent for the very weak emission occurring in the region of 250–350 K. The lifetime for this weak emission at 250 K is approximately 2 μs. As the temperature is lowered to the point where the sample begins to strongly emit (~170 K), the lifetime drops to 100 ns! Furthermore, the apparent radiative rate constant in the high-temperature region is evaluated as only 400 $s^{-1}$, a very improbable value compared to the usual $10^4$–$10^5$ values.[2,8] In light of these results, we suggest that the previously reported emission in the high-temperature region is due to trace impurities of some other emissive ruthenium complex (i.e., $Ru(bpy)_3^{2+}$) and that both Ru-

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**Table I.** Parameters for Several Polypyridine Complexes Based upon Emission Intensity and Lifetimes

| complex | method[a] | *A*[b] | *B*[c] | $\Delta E$, cm$^{-1}$ | $\phi_{ic}$(298 K)[d] | $\phi_{ic}$(220 K)[d] |
|---|---|---|---|---|---|---|
| $Ru(bpy)_3^{2+}$ | L | $3.9 \times 10^5$ | $1.9 \times 10^{14}$ | 3859 | 0.79 | 0.0049 |
| | I | 7.86 | $1.56 \times 10^9$ | 3951 | | |
| $Ru(bpy)_2diaz^{2+}$ | L | $3.1 \times 10^5$ | $8.5 \times 10^{14}$ | 2271 | 0.99998 | 0.9991 |
| | I | 5.5 | $1.7 \times 10^9$ | 1846 | | |
| $Ru(bpy)_2(py)_2^{2+}$ | L | $4.23 \times 10^5$ | $2.34 \times 10^{14}$ | 2758 | 0.9989 | 0.890 |
| | I | 21.0 | $1.35 \times 10^8$ | 1957 | | |

[a] Based upon lifetimes (L) or intensity (I) measurements. [b] $k_r + k_{nr}$ for L and $(k_r + k_{nr})/k_r$ for I. [c] $k_0$ for L and $k_0/k_r$ for I. [d] Quantum yield of LF production at 298 and 220 K.

$(bpy)_2diaz^{2+}$ and $Ru(bpy)_2(py)_2^{2+}$ are essentially nonemissive above 230 K. Indeed, the amount of luminescence at 298 K decreased after repeated recrystallization although it did not completely disappear even after seven recrystallizations. Balzani and co-workers have reached a similar conclusion about luminescent impurities and suggest that most reported cases of dual luminescence are due to these impurities.[11]

The emission intensities and lifetimes for $Ru(bpy)_3^{2+}$, $Ru(bpy)_2diaz^{2+}$, and $Ru(bpy)_2(py)_2^{2+}$ have been fit to eq 1, and the results are shown in Table I. For the latter two complexes, only values at or below 200 K were used in this fitting procedure. The results obtained for $Ru(bpy)_3^{2+}$ agree with previous reports.[4,12,13] Furthermore, the activation energy obtained from the temperature dependence of both the emission intensity and lifetime agree within experimental error.

The values of $\Delta E$ for $Ru(bpy)_2diaz^{2+}$ and $Ru(bpy)_2(py)_2^{2+}$ are substantially lower than the corresponding value for $Ru(bpy)_3^{2+}$. In both cases, these results agree with the postulates of ligand field theory. Pyridine and diazafluorene are known to be lower than bipyridine in the spectrochemical series.[6] Hence, substitution of these ligands for bpy results in a decreased ligand field and, therefore, a lower LF excited-state energy. Since the $^3$MLCT excited state is not significantly affected, the variation in the LF state dictates the energy gap.

The anticipated lifetime of the $^3$MLCT state at 298 K can be evaluated for both $Ru(bpy)_2diaz^{2+}$ and $Ru(bpy)_2(py)_2^{2+}$ with the aid of eq 1 and the parameters in Table I. The resulting values are 0.07 and 2.7 ns, respectively. With these extremely short lifetimes, the $^3$MLCT excited state is not likely to be involved in any bimolecular processes at this temperature. This expectation is confirmed by the fact that no photooxidation of these two Ru(II) complexes to the corresponding Ru(III) complexes could be observed even at high concentrations of persulfate.[14]

Another interesting fact is apparent from Table I; the activation energies for $Ru(bpy)_2diaz^{2+}$ and $Ru(bpy)_2(py)_2^{2+}$ obtained from emission intensity measurements are lower than those obtained from lifetimes measurements. Such is not the case for $Ru(bpy)_3^{2+}$. The exact cause of this behavior is at present not known. One possible explanation is an *apparent* temperature dependence of $k_r$. This may be induced by temperature-dependent intersystem crossing from $^1$MLCT directly to the (presumably triplet) LF state. The energy lowering of the LF state may facilitate this conversion. In fact, Nakamara has recently suggested that an apparent decrease in $k_r$ as 3,3′-dimethyl-2,2′-bipyridine (DMB) replaces bipyridine in $RuL_3^{2+}$ complexes is related to changes in the intersystem crossing efficiency.[15] Due to steric effects, DMB is a weaker ligand than bpy so that the LF state will be lowered as DMB ligands replace bpy. This may facilitate intersystem crossing to the LF state. Further experiments designed to address this problem are currently under way.

**Acknowledgment.** R.H.S. thanks the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. W.R.C. acknowledges the support of the National Science Foundation (Grant CHE-8205698) and the LSU Center for Energy Studies, under U.S. Department of Energy Grant No. DE-FG-0580ER1019F. The technical assistance of R. Zinn in the curve-fitting procedure is gratefully acknowledged.

**Registry No.** $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(bpy)_2diaz^{2+}$, 91606-22-3; $Ru(bpy)_2(py)_2^{2+}$, 47779-80-6.

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