as NC = TOT − 2(BG1 + BG2), where TOT is the estimated peak intensity.

The intensities of four standard reflections, at 100-reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects and then for absorption (minimum transmission factor 0.46, maximum 0.78), resulting in 2038 reflections of which 1404 had ${F_o}^2 > 3\sigma({F_o}^2)$, where $({F_o}^2)$ was estimated from counting statistics ($p = 0.03$).[26] Only these latter data were used in the final refinement of the structural parameters.

Solution and Refinement of the Structure. Full-matrix least-squares refinement was based on F, and the function minimized was $w(|F_o| - |F_c|)^2$. The weights w were taken as $[2F_o/\sigma({F_o}^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[27] and those for hydrogen from Stewart et al.[28] The effects of anomolous dispersion for all nonhydrogen atoms were included in F with use of the values of Cromer and Ibers[29] for $\Delta f'$ and $\Delta f''$.

The position of the Br atom was determined from a three-dimensional Patterson function calculated from all the intensity data. The intensity data were phased sufficiently well by these positional coordinates that difference Fourier syntheses revealed most of the nonhydrogen atoms, the remaining nonhydrogen atoms being inserted in calculated positions. Most of the cage hydrogen atoms were found from a Fourier difference map after introducing anisotropic thermal parameters for all nonhydrogen atoms. At least one hydrogen on each methyl group was found; the remaining hydrogen positions were calculated and inserted. The hydrogen atoms were included in the refinement for three cycles and thereafter held fixed. A final Fourier difference map was featureless. The error in an observation of unit weight was 1.96, and the largest parameter shift in the last cycle of refinement was 0.25 times the estimated standard deviation.

The model converged with $R = 0.057$ and $R_w = 0.063$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. Tables of observed and calculated structure factors are available (see paragraph at end of paper on supplementary material). The computing system and programs are described elsewhere [30]

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Supplementary Material Available: Listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Excited States of Mixed-Ligand Chelates of Ruthenium(II). Quantum Yield and Decay Time Measurements[1a]

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Abstract: The photoluminescence of a series of $[\mathrm{Ru(II)(bpy)}_m(\mathrm{N{-}N})_n]^{2+}$ cations [$m = 3 - n$; $n = 0, 1, 2, 3$; bpy = 2,2′-bipyridine; N–N = 1,10-phenanthroline (phen) or substituted phen or substituted bpy] was investigated. All compounds displayed a prominent visible luminescence, a single ~1.3 kK vibration progression, and an ~5 μs decay time at 77 K that increased monotonically as the temperature was lowered. Quantum yields at 77 K ranged between 0.35 and 0.58. The data were analyzed in terms of a charge-transfer-to-ligand excited manifold of three levels.

Ruthenium(II) complexes containing π-conjugated ligands have become the focus of a variety of photochemical,[2] electrochemical,[3] and spectroscopic investigations.[4,5] The fascination is elicited by the occurrence of charge-transfer-to-ligand (CTTL) excited states that endow the complexes with rich visible absorption spectra and, when the ligand field strengths are sufficiently high, with a visible luminescence that can be stimulated in a variety of ways. Moreover, these complexes display luminescence in fluid solution. Thus, they possess important measurable physical parameters that can add insight to mechanistic considerations of photophysical and photochemical processes.[6] In addition to the lively fundamental interest generated by these materials in the field of excited state chemistry, a further impulse to investigate them is occasioned by the circumstance that they not only absorb visible light but are theoretically capable of splitting water into its elements by the utilization of solar energy.[7]

Our interest in Ru(II) complexes has evolved from the intention to provide physical and mathematical models of the excited states of transition metal complexes based on photophysical measurements. For these studies, extending over a decade, Ru(II) complexes with 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) ligands have played a pivotal role because the $(4d)^6$ strong-field configuration and the low-lying ligand π* orbitals provide the proper disposition of energy levels such that intense emission occurs from excited states that are clearly charge transfer to ligand in nature. This luminescence has provided the tool to probe the innate properties of CTTL states and has led to a coherent description of them that can, we conjecture, be applied with some confidence to CTTL states exhibited by complexes of other elements and other electronic configurations.[4,5]

Recently, we have completed our investigations of the analogous complexes of Os(II) and have given a description of the CTTL

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excited states of these molecules that closely parallels the one published previously for Ru(II).[8,9] We have accumulated evidence that our picture of CTTL excited states can be extended to related complexes of Ir(III) $(5d)^6$ also.[10]

The mathematical model of CTTL excited states proposed for diamagnetic symmetrical (D_3) $(nd)^6$ $(n = 4, 5)$ complexes with π-conjugated ligands has been thoroughly described elsewhere.[11] An essential feature is the stipulation of strong ligand–ligand coupling that occurs through $d\pi^*$ interaction with the metal. Moreover, to conform to the number, disposition, and radiative properties of the lowest lying states, as revealed by detailed measurements on the luminescence, we have been led to assign the lowest CTTL configuration, from which these states arise, to $d\pi^*(a_2)$. Thus, we visualize this lowest excited configuration as one in which an electron has been essentially promoted from the central metal core to an antibonding orbital of a_2 symmetry (D_3) *delocalized over the ligand system*. Indeed, the diffusion of the optical electron over all the ligands in these excited states not only rationalizes the spectroscopic data but also, along with spin–orbit coupling, plays a fundamental role in the mathematical quantification of the model.

During the many studies we carried out on Ru(II) complexes of D_3 symmetry, we were able to discern an influence on the excited states by substituents on the ligands only when they were in the 4,7 positions of the 1,10-phenanthroline. We were led to the conclusion that the promoted electron in the $d\pi^*$ configuration spends most of its time on the nitrogen atoms adjacent to the metal. This conclusion was also reached for the corresponding Os(II) complexes.[8,9] Moreover, for the *cis*-$[Os(py)_2(bpy)_2]^{2+}$ ion, which possesses C_2 symmetry, both the absorption and emission spectra closely resemble those exhibited by $[Os(bpy)_3]^{2+}$, a cation of D_3 symmetry. Thus, the electronic symmetry appears to be higher than the geometrical symmetry in this *cis*-pyridine complex, at least as far as the spectra can be analyzed. For *cis*-$[Ru(CN)_2(phen)_2]$, however, the data from the temperature dependence of the decay times cannot be adequately treated with a model imposing D_3 symmetry, and lower symmetry must be invoked.[12]

The following question naturally arises. What magnitude of perturbation must be introduced into a cis complex displaying charge-transfer emission in order for our measurements to reveal electronic dissymmetry? In particular, the assignments we have inferred from our optical measurements for the lowest $d\pi^*$ excited states of D_3 complexes of Ru(II) and Os(II) attribute the origin of the luminescence to a manifold of three levels of A_1, E, and A_2 symmetry in order of increasing energy. For a cis complex, no degeneracies are theoretically possible and a four-level system should arise, just as our data on the dicyano complexes of Ru(II) require. In the current study we report new optical investigations of seven complexes of Ru(II) that exhibit intense photoluminescence. While preserving at all times the essential nitrogen atom microsymmetry about the Ru(II) ion, we have upset the total geometrical symmetry both in delicate and in robust ways and have searched within the optical data for manifestations of electronic dissymmetry in the $d\pi^*$ configuration.

Experimental Section

Syntheses, Purifications, and Analyses. All syntheses were carried out with the use of reagent grade materials. The $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ and the substituted ligands, 4,4′-dimethyl-2,2′-bipyridine (4,4′-Me_2bpy), 4,4′-diphenyl-2,2′-bipyridine (4,4′-Ph_2bpy), 5,6-dimethyl-1,10-phenanthroline (5,6-Me_2phen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen), and 4,7-diphenyl-1,10-phenanthroline (4,7-Ph_2phen), were purchased from G. Frederick Smith Chemical Co. and used without further purification. The preparations of $[Ru(bpy)_2(phen)]Cl_2$, $[Ru(bpy)(phen)_2]Cl_2$, $[Ru(phen)_3]Cl_2$, and the starting materials were described previously;[13] this cited reference includes detailed procedures for the preparation and purification of mixed chelates of the general type reported here. In addition to the chloride salts, the hexafluorophosphate salts were made in most cases to assist in establishing the stoichiometries of the cations. The elemental analyses were done by the University of Idaho and Galbraith Laboratories, Inc.

Table I. 60 MHz ^{1}H NMR Spectra of the Ruthenium(II) Mixed Chelates in D_2O[a]

complex[b]	–CH=[c]	$-CH_3$
$[Ru(bpy)_3]^{2+}$	480	
$[Ru(bpy)_2(4,4'\text{-}Me_2bpy)]^{2+}$	526 (22.4)	178 (6)
$[Ru(bpy)_2(4,4'\text{-}Ph_2bpy)]^{2+}$	530	
$[Ru(bpy)_2(phen)]^{2+}$	533	
$[Ru(bpy)_2(5,6\text{-}Me_2phen)]^{2+}$	528 (22.0)	169 (6)
$[Ru(bpy)_2(4,7\text{-}Me_2phen)]^{2+}$	527 (21.8)	195 (6)
$[Ru(bpy)_2(4,7\text{-}Ph_2phen)]^{2+}$	552	
$[Ru(bpy)(phen)_2]^{2+}$	524	
$[Ru(phen)_3]^{2+}$	548	

[a] Values in Hz downfield from DSS. Peak area in parentheses. [b] Chloride salts. [c] Approximate center of complex multiplet.

Anal. $[Ru(bpy)_2(4,4'\text{-}Me_2bpy)]^{2+}$: Calcd for $[Ru(C_{10}H_8N_2)_2(C_{12}H_{12}N_2)]Cl_2{\cdot}2H_2O$: C, 54.55; H, 4.58; Cl, 10.06; N, 11.94. Found: C, 54.90; H, 4.71; Cl, 10.34; N, 12.00. Calcd for $[Ru(C_{10}H_8N_2)_2(C_{12}H_{12}N_2)](PF_6)_2{\cdot}H_2O$: C, 41.91; H, 2.82; N, 9.28. Found: C, 42.47; H, 3.03; N, 8.99. $[Ru(bpy)_2(4,4'\text{-}Ph_2phen)]Cl_2$: Calcd for $[Ru(C_{10}H_8N_2)_2(C_{22}H_{16}N_2)]Cl_2{\cdot}2H_2O$: C, 60.87; H, 4.14; Cl, 8.56; N, 10.14. Found: C, 61.22; H, 4.48; Cl, 8.10; N, 10.10. $[Ru(bpy)_2(5,6\text{-}Me_2phen)]^{2+}$: Calcd for $[Ru(C_{10}H_8N_2)_2(C_{14}H_{12}N_2)]Cl_2{\cdot}7H_2O$: C, 49.88; H, 5.17; Cl, 8.66; N, 10.26. Found: C, 50.27; H, 4.27; Cl, 9.77; N, 10.30. Calcd for $[Ru(C_{10}H_8N_2)_2(C_{14}H_{12}N_2)](PF_6)_2{\cdot}{}^1/_2H_2O$: C, 44.36; H, 3.18; N, 9.13. Found: C, 44.59; H, 2.99; N, 9.03. $[Ru(bpy)_2(4,7\text{-}Me_2phen)]^{2+}$: Calcd for $[Ru(C_{10}H_8N_2)_2(C_{14}H_{12}N_2)]Cl_2{\cdot}2H_2O$: C, 56.04; H, 4.43; Cl, 9.73; N, 11.53. Found: C, 55.41; H, 4.37; Cl, 9.70; N, 11.59. Calcd for $[Ru(C_{10}H_8N_2)_2(C_{14}H_{12}N_2)](PF_6)_2{\cdot}2H_2O$: C, 43.09; H, 3.40; N, 8.87. Found: C, 42.71; H, 2.97; N, 8.91. $[Ru(bpy)_2(4,7\text{-}Ph_2phen)]^{2+}$: Calcd for $[Ru(C_{10}H_8N_2)_2(C_{24}H_{16}N_2)]Cl_2{\cdot}3H_2O$: C, 60.69; H, 4.40; Cl, 8.14; N, 9.65. Found: C, 61.04; H, 4.17; Cl, 8.38; N, 9.64. Calcd for $[Ru(C_{10}H_8N_2)_2(C_{24}H_{16}N_2)](PF_6)_2{\cdot}H_2O$: C, 50.15; H, 3.25; N, 7.98. Found: C, 50.41; H, 3.13; N, 7.80.

^{1}H NMR Spectra. A complex that contained a ligand substituted with a methyl group gave a ^{1}H NMR spectrum that revealed only a single resonance in the methyl region with a relative area (methyl to methylene) consistent with that expected for a complex of C_2 symmetry substituted in the desired stoichiometry of 2:1 (see Table I). The ^{1}H NMR spectra were obtained on a Varian Model HA-60. Sodium (3-trimethylsilyl)-propanesulfonate (DSS) was employed as an internal standard. The chemical shifts were all estimated in hertz downfield from DSS.

Spectroscopic Measurements. Absorption spectra were taken on a Cary Model 14 spectrophotometer. Emission spectra from samples maintained at 77 K in a 4:1 (v/v) ethanol–methanol glass were monitored with a near-IR spectrofluorimeter described elsewhere.[14] The spectra, stimulated by broad-band near-UV radiation, are shown in Figure 1. They have been corrected for the wavelength dependence of the instrument response. Quantum efficiencies[15] and temperature-dependent lifetimes[4] were measured as previously described. For the latter determination, instead of employing a sample dissolved in plastic we employed 4:1 ethanol–methanol glass solutions contained in a custom designed sample holder. Each experimentally measured lifetime used in the subsequent data analysis was the average of at least five measurements. At both 77 and 4.2 K the luminescent decays were exponential over three lives for all the complexes studied and, even at the lowest temperatures reached (~1.7 K), the lifetimes maintained their exponentiality within the accuracy of the measurements.

Results

The results of the emission, quantum yield, and decay time measurements are represented in Figure 1 and Table II. The luminescence from each molecule clearly consists of a relatively diffuse electronic band envelope displaying a single (~1.3 kK) vibrational progression. As shown in Table II the quantum yields at 77 K are substantial, and they fall within a relatively narrow range (0.35–0.58). The luminescence is correspondingly bright

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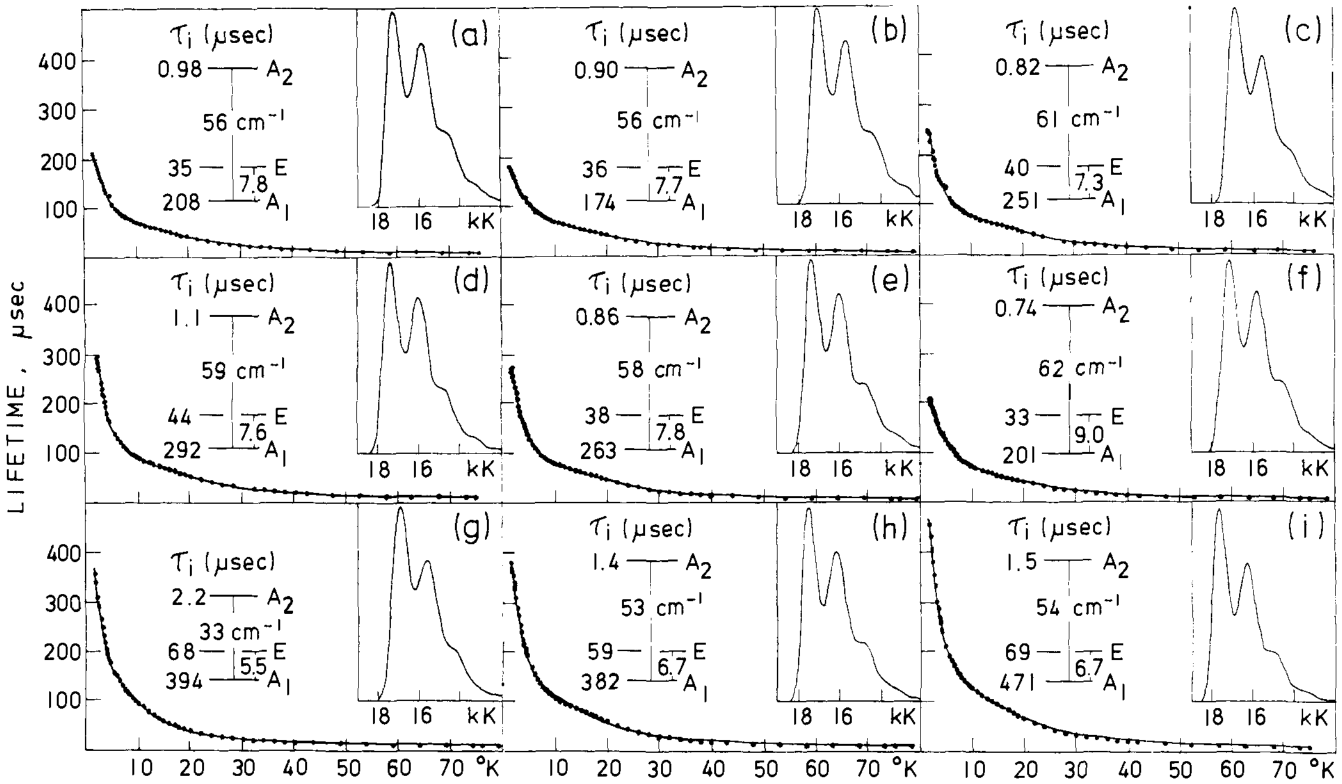

Figure 1. Emission spectra (77 K), lifetimes, and excited state parameters for ruthenium(II) complexes: (a) $[Ru(bpy)_3]Cl_2$, (b) $[Ru(bpy)_2(4,4'\text{-}Me_2(bpy)]Cl_2$, (c) $[Ru(bpy)_2(4,4'\text{-}Ph_2bpy)]Cl_2$, (d) $[Ru(bpy)_2(phen)]Cl_2$, (e) $[Ru(bpy)_2(5,6\text{-}Me_2phen)]Cl_2$, (f) $[Ru(bpy)_2(4,7\text{-}Me_2phen)]Cl_2$, (g) $[Ru(bpy)_2(4,7\text{-}Ph_2phen)]Cl_2$, $[Ru(bpy)_2(4,7\text{-}Ph_2phen)]Cl_2$, (h) $[Ru(bpy)(phen)_2]Cl_2$, (i) $[Ru(phen)_3]Cl_2$. Group theoretical assignments based on D_3 symmetry.

at 77 K, but the intensity falls off monotonically with decreasing temperature until, at the lowest temperature reached (~1.7 K), the intensity is ~10% of the 77 K value.

The temperature dependences of the decay times all display a similar profile. As the temperature is lowered, the lifetimes increase monotonically from a few microseconds at 77 K to well over 100 μs at the lowest temperatures reached. The measured decay times at the two fixed points (77 and 4.2 K) are included in Table II.

Discussion

Model for the Excited State Manifold. The exceptional similarity of all the spectra reproduced in Figure 1, the uniformity of the decay-time–temperature curves, and the comparable magnitudes of the measured quantum yields clearly dictate a dπ^* configurational assignment for the luminescing states in concert with all the previous luminescence work on the complexes of Ru(II). Furthermore, the data clearly dictate a *multistate* model for the origin of the emission. If a single state, or group of degenerate states, were responsible for the luminescence, the τ/ϕ ratio should be temperature independent and equal the limiting lifetime, a fundamental molecular property, for the system at low temperature. Yet, as shown in Table II, the *measured* life at 4.2 K exceeds this value by a factor of 10 for all the complexes. Since the intensity at 4.2 K, and by inference the quantum yield, is substantially smaller than the value measured at 77 K, the estimated value for τ/ϕ at 4.2 K is ~15 times the 77 K value. To ratonalize this behavior we are led inexorably to a multiple state model for the origin of the emission. Furthermore, because the observed decay times are exponential at all times and temperatures, we postulate that the manifold of emitting states maintains thermal equilibrium throughout the decay process.

As developed elsewhere,[4,12] these physical assumptions for the emitting manifold lead to the expression

$$\tau_m(T) = \frac{1 + 2e^{-\Delta\epsilon_1/kT} + e^{-\Delta\epsilon_2/kT}}{(1/\tau_1) + (2/\tau_2)e^{-\epsilon_1/kT} + (1/\tau_3)e^{-\Delta\epsilon_2/kT}}$$

for the temperature dependence of the measured decay time of each complex. For any fixed temperature an exponential decay is predicted. If we stipulate further, however, that the rate

Table II. Emission Energies, Quantum Yields, and Lifetimes of Ruthenium(II) Complexes in 4:1 (v/v) Ethanol–Methanol

complex	ν(77 K), cm^{-1} × 10^{-3}	ϕ(77 K)	τ(77 K), μs	τ(~4.2 K), μs	τ(77 K)/ ϕ(77 K)
$[Ru(bpy)_3]Cl_2$	17.23 15.88 14.69	0.38[a]	5.2	129	13.7
$[Ru(bpy)_2(4,4'\text{-}Me_2bpy)]Cl_2$	17.06 15.70 14.40	0.35	5.2	116	14.8
$[Ru(bpy)_2(4,4'\text{-}Ph_2bpy)]Cl_2$	16.85 15.51 14.25	0.46	5.6	144	12.2
$[Ru(bpy)_2\text{-}(phen)]Cl_2$	17.40 16.02 14.80	0.44	6.6	166	15.0
$[Ru(bpy)_2(5,6\text{-}Me_2phen)]Cl_2$	17.32 15.97 14.75	0.42	6.1	154	14.5
$[Ru(bpy)_2(4,7\text{-}Me_2phen)]Cl_2$	17.15 15.84 14.70	0.38	5.6	140	14.7
$[Ru(bpy)_2(4,7\text{-}Ph_2phen)]Cl_2$	16.98 15.65 14.30	0.54	9.4	189	17.4
$[Ru(bpy)\text{-}(phen)_2]Cl_2$	17.56 16.12 14.99	0.56	9.1	203	16.3
$[Ru(phen)_3]Cl_2$	17.64 16.28 14.99	0.58[a]	9.8	242	16.9

[a] From ref 15.

constants and energy gaps in the equation are temperature-independent quantities, then a computer fit of the observed τ vs. T curve to the equation produces sets of levels and rate constants for the manifold of excited states. We have accomplished this computer fitting for all the complexes and included the results in Figure 1. The derived sets of levels and rate constants are remarkably similar and represent, we believe, invariant molecular parameters. Thus, there appear to be no essential differences between the excited state manifolds of the D_3 species and those of lower geometrical symmetry. Within the accuracy of our measurements the behavior is identical. Therefore, we have explicitly included the degeneracy factor of 2 in the second level of all the complexes as required by our theoretical model for D_3 systems.[11] Mathematically, the factor is not required to fit the data. Its inclusion here reflects our confidence in the previous assignments of the three lowest levels in the D_3 species and our inability to detect any splitting of the E level in the compounds of lower geometrical symmetry, although, theoretically, a mixed-ligand complex should possess no degenerate levels at all.

Search for Electronic Dissymmetry. We have sifted our optical data for manifestations of electronic dissymmetry in the excited state manifold responsible for the luminescence. With the possible exception of the two complexes containing the ligand substituted in the 4,7 positions, there is no evidence for a distortion of the two energy gaps away from the values obtained for the two parent trigonal molecules. A perusal of the rate constants in Figure 1 also reveals no trend in the values that reflects a symmetry change. The lowest level, assigned as A_1 in D_3 and therefore dipole forbidden in the tris species, correlates into B in the group C_2 and thus becomes formally allowed. Yet, the τ_1 values for the seven mixed-ligand chelates give no indication that this lowest level has acquired any allowed character. For the upper two levels assigned to the dipole-allowed E and A_2 states in D_3, one would not expect to see any effects of subtle changes in symmetry and, indeed, none are apparent. These statements hold for the two complexes containing the 4,7-substituted phen ligand also, a disappointing result since the energy level gaps of these two species seem to indicate some dissymmetry.

Reliability of Excited State Parameters. Our methods of extracting rate constants and energies of activation from computer fits of τ vs. T curves have been described elsewhere.[4] We have also discussed our inability to assess the accuracy of these procedures.[4,12] Pertinent to the current study is the restriction of the τ equation to three levels. Our data on all the D_3 compounds of Ru(II) displaying CT luminescence that we have accumulated cannot be fit satisfactorily at all by an expression restricted to two levels (three parameters). We find here that the mixed-ligand complexes display τ vs. T behaviors that require only a three-level (five-parameter) model also. A necessary extension to four levels (seven parameters) was originally anticipated because of the lower geometrical symmetry of the mixed-ligand molecules, but no such extension was required. In fact, when the experimental data of Figure 1 are fit to a four-level expression, there is no significant improvement whatever in the goodness of fit as revealed by the residues of the minimization procedure. Only three levels are needed. Thus, we are left with the following alternatives: (a) the cis systems are displaying an essentially trigonal D_3 electronic symmetry in the excited states that is higher than the geometrical symmetry; (b) all the systems, *including those with three identical ligands*, possess a four-level excited state manifold, as expected for C_2 symmetry, and one of the levels is too high to be populated significantly within the accessible temperature range; (c) our methods are just too crude to distinguish between a three- and four-level model; or (d) the assumptions behind the model and fitting procedure are invalid. We rule out the last alternative because of the manifest success we have had for a host of Ru(II) and Os(II) complexes in which both decay times and quantum yields have been fit to the same set of levels, a procedure that demands a great deal of the proposed model, and the latter has withstood the test. Point (c) cannot be summarily dismissed, for we have always deliberately chosen the minimum number of levels necessary to rationalize the data. For D_3 complexes the experimental requirement of three levels is nicely substantiated by theory.[11] Evidence against alternative (c) lies in the data of Figure 1 also. For a complex, such as $[Ru(bpy)_2(4,4'\text{-}Me_2bpy)]^{2+}$, where little distortion from trigonal symmetry in the excited state is expected, we see nothing in the data that distinguishes it from a species, such as $[Ru(bpy)_2(phen)]^{2+}$, where more electronic dissymmetry is expected. Evidence that our methods do reveal electronic dissymmetry when the odd ligand(s) is substantially different than the other two comes from two sources, the $Ru(CN)_2(bpy)_2$ molecule[12] and several $IrCl_2(N\text{-}N)_2$ analogues where N–N is bpy or substituted bpy.[10] Our decay time and quantum yield studies of the CT luminescence from these systems cannot be fit by a three-level scheme except by truncation of the temperature range. We accept this as strong evidence that our methods do distinguish three- and four-level excited manifolds when structural distortion is substantial. We have also found systems where only two levels are expected theoretically and, indeed, two are all that the fitting procedure demands.[16]

For the two molecules containing the 4,7-phen moiety, the evidence is confusing. The energy-level gaps appear to reflect a perturbation due to the substituents on the unique ligand. This would necessarily mean a lowering of the electronic symmetry. The lifetime of the lowest level, however, does not shorten and thus reflect any lowering of symmetry. There is also no evidence that a fourth level is required to rationalize their data. Three are both necessary and sufficient.

Conclusion

From these current studies and the previous published work on Ru(II) complexes we draw the following conclusions: (a) The lowest excited configuration in all the molecules is $d\pi^*$ in nature. (b) The emission originates within a manifold of three excited states that span $\sim 60\ \text{cm}^{-1}$ and are in Boltzmann equilibrium. (c) The temperature dependence of the decay time is due to population redistribution among levels that possess temperature-independent rate constants.

Within the accuracy of our measurements for the mixed-ligand complexes of the general formula $[Ru(bpy)_m(N\text{-}N)_n]^{2+}$ where N–N is a phen, a substituted-phen, or a substituted-bpy ligand and m, n = 2, 1 or 1, 2, we cannot distinguish between two plausible alternatives. Either (1) the electronic symmetry in the excited $d\pi^*$ manifold is essentially trigonal for all the systems, including those with nonequivalent ligands, or (2) all the molecules, including those with formally D_3 symmetry (three identical ligands), are substantially distorted in the excited $d\pi^*$ configuration. If we choose the first alternative, then the electronic properties of the excited states are best described as weighted averages of the properties of the individual ligands as we have previously proposed.[13] Evidently, in the excited configuration the promoted electron is essentially localized on the nitrogen orbitals adjacent to the metal atom. The influence of the rest of the ligand framework is felt in a second-order way through the quenching phenomenom. Choosing the second alternative means that excitation to the $d\pi^*$ configuration leaves the molecule in a distorted geometry, with the electronic charge distribution skewed toward one ligand. Evidence for this interpretation has been acquired by Dallinger and Woodruff[17] with the use of the resonance Raman effect. Excited state distortion is also indicated by the polarization ratios obtained by DeArmond et al.[18] The resonance Raman data are acquired in a time scale (ns) much shorter than ours and in fluid solution. The polarization data are taken on our time scale in glass matrices and thus relate directly to the studies reported here. We remark that the issue of distortion may be related to the degree of sensitivity of the measured parameters to the wave functions. Our fitting procedure yields energy separations that appear to approximate molecular invariants. Small distortions

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could dictate gross changes in the polarization ratios while producing only small changes in the state energies. Our basic description based on trigonal symmetry with a substantial amount of spin–orbit coupling included in the core Hamiltonian may only be adequate to rationalize properties related to energy. A definitive answer to the question of the electronic symmetry awaits the measurement of more indicators, particularly polarization ratios, on more molecules with subtle, progressive changes in symmetry.

Preparation of Zirconium(II) Complexes by Ligand-Induced Reductive Elimination. Bis(η^5-cyclopentadienyl)bis(phosphine)zirconium(II) Complexes and Their Reactions

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Abstract: Bis(η^5-cyclopentadienyl)bis(phosphine)zirconium(II) complexes were prepared by ligand-induced reductive elimination of alkane from bis(η^5-cyclopentadienyl)chloroalkylzirconium(IV) precursors. Reactions of these species with H_2, CO, other phosphines, acetylenes, olefins, arenes, and organic halides are described.

The group 4 metallocenes are electron-deficient (14-electron) coordinatively unsaturated species which are kinetically and thermodynamically unstable to oxidation.[1] Two-electron reduction of the metallocene dichlorides with use of alkali metals or aromatic anions,[2] Grignard reagents,[3] or electrochemical methods[4] may initially yield a simple metallocene, but under the reaction conditions it deactivates by intermolecular insertions into activated C–H bonds, giving dimers, polymers, or species incorporating exogenous ligands.[5]

Intermolecular, and ultimately irreversible, deactivation of titanocene is suppressed in permethylated cyclopentadienyl derivatives which undergo *reversible* intramolecular C–H insertion and react preferentially with most substrates from the low-valent Ti(II) tautomer.[5b,6] With the use of this system, the role of reduced Ti in molecular nitrogen fixation has been clearly defined, and extensions of this work have shown that the chemistry of low-valent Zr is equally interesting.[7]

Apart from the results of these investigations, the chemistry of low-valent Zr is poorly understood. The lack of readily accessible low-valent Zr compounds restricts the range of available synthetic transformations to manipulation of ligands on a Zr(IV) d^0 center.[1] Catalytic cycles employing lower oxidation states of Zr or the synthesis of new Zr compounds by the oxidative processes commonly used for other transition-metal complexes are rare. A practical example of this limitation is that Zr(IV) alkyl and alkenyl compounds, which are useful intermediates in organic synthesis,[8] are accessible only by hydrozirconation or by alkylation of Zr(IV) compounds with a suitable main-group organometallic.[1,8]

Kinetic stabilization of low-valent Zr can be achieved in electronically saturated (18-electron) complexes of π-acceptor ligands, as recent syntheses of bis(η^6-arene)(PMe$_3$)Zr^0 (ref 9), (η^5-C$_6$H$_8$)(dmpe)$_2$(H)Zr^{II} (ref 10), and bis(η^4-C$_4$H$_6$)(dmpe)(PMe$_3$)Zr^0 (ref 10) have demonstrated.[7] The simple metallocene derivative Cp$_2$Zr(CO)$_2$ has been prepared by reduction of Cp$_2$ZrCl$_2$ under carbon monoxide,[11] but this complex is remarkably unreactive.[11c]

We have found that certain donor ligands induce reductive elimination of alkane from alkylbis(η^5-cyclopentadienyl)hydrozirconium(IV) complexes.[12] With use of tertiary phosphines in this reaction, bis(η^5-cyclopentadienyl)bis(phosphine)zirconium(II) complexes are produced in high yield with alkane as the only byproduct. This synthetic method may be successful because it avoids direct generation of the 14-electron metallocene, Cp$_2$Zr. A preliminary account of this work has appeared,[12c] and we now report details for the preparation of these Zr(II) bis(phosphine) complexes and some of their simple synthetic applications, which demonstrate their utility as highly reactive functional equivalents of monomeric "zirconocene".

Results and Discussion

Preparation and Characterization of Zr(II) Bis(phosphine) Complexes. (Cyclohexylmethyl)bis(η^5-cyclopentadienyl)hydrozirconium(IV) (**1a**) reacts rapidly with tertiary phosphines to

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