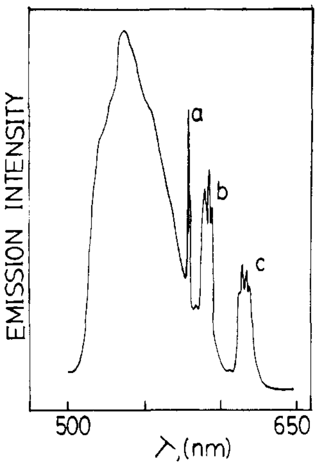

Figure 2. Emission spectrum of Eu^{3+}–A zeolite at 4 K (excitation wavelength 425 nm): (a) $^5D_0 \rightarrow {}^7F_0$ transition; (b) $^5D_0 \rightarrow {}^7F_1$ transition; (c) $^5D_0 \rightarrow {}^7F_2$ transition.

the same ions in the pores of ZSM-5 and Y. Diffusion in Y appears to be greater than that in ZSM-5. This is consistent with the sizes of the pores of these zeolites.

Evidence of association between europium(III) and uranyl ions was obtained, however, when the uranyl- and europium(III)-exchanged Y zeolite was thermally treated to 350 °C. The intention of this experiment was to move the europium(III) ions into the sodalite cages from the supercage and then observe the effect of the energy-transfer efficiency. After thermal treatment the uranyl moiety was decomposed, as evidenced by a very weak excitation and emission spectrum. This was surprising since thermal treatment of UO_2–$Y^{5,6}$ zeolite produces a stable luminescent uranyl–Y zeolite that, when rehydrated, can regenerate the starting material. Thermal treatment[15] of Eu(III)Y to 375 °C also produces a stable material. The above observation must mean that uranyl and europium(III) ions react with one another perhaps by an inner-sphere mechanism during thermal treatment. Bridging hydroxyl uranyl/europium(III) oligomers in aqueous solution[16] have indeed been suggested recently.

For systems in which there is only type of Eu^{3+} binding site, the $^5D_0 \rightarrow {}^7F_1$ europium transition at 595 nm and the $^5D_0 \rightarrow {}^7F_2$ europium transition at 615 nm split into three and five peaks, respectively, under high-resolution conditions.[14] Group-theoretical calculations indicate that the site must be of C_2 or lower symmetry if these splittings are observed. The emission spectrum in Figure 2 of UO_2^{2+},Eu^{3+}–A zeolite at 4 K under high resolution indicates that the europium(III) ion is likely in a symmetry of at least C_2 or lower due to the number of splittings observed. The transition at 595 nm splits into three peaks, and the 615-nm transition does not split but has some shoulders. Another criterion for single siting is that the $^5D_0 \rightarrow {}^7F_0$ europium peak at 580 nm must not split. This is also true for the A zeolite system. This europium ion site must be in the supercage of zeolite A. EXAFS and luminescence lifetime measurements[8e,25] indicate that the europium(III) ion site has three water molecules and three framework oxygen atoms. The efficiency of energy transfer is noticeably reduced at this temperature. These results suggest that energy transfer in the material derived from zeolite A proceeds via a long-range mechanism.

Energy transfer in these zeolites occurs betwen the $\Omega = 4$ level of UO_2^{2+} and the group of Eu^{3+} levels $^5D_2$, $^5D_3$, and $^5L_6$.[16] Phonon-assisted processes are possible[16,26] since some of these levels are higher than the $\Omega = 4$ level. It is exciting that the efficiency of energy transfer can be controlled by the method of preparation and by the structural framework of the particular zeolite. These observations imply that solution-like environments do exist in zeolites and that fundamental photochemical processes like energy transfer that abound in solution can also occur to a certain extent in zeolite molecular sieves.

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Registry No. UO_2^{2+}, 16637-16-4; Eu^{3+}, 22541-18-0.

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Luminescence of Ruthenium(II) Tris Chelate Complexes Containing the Ligands 2,2′-Bipyridine and 2,2′-Biisoquinoline. Behavior of the $Ru(bpy)^{2+}$ and $Ru(bpy)_2^{2+}$ Emitting Units

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The absorption spectra, emission spectra, emission lifetimes, and the temperature dependence of the emission intensity and lifetime (between 84 and 330 K) of the complexes $Ru(bpy)_2(i\text{-biq})^{2+}$, $Ru(bpy)(i\text{-biq})_2^{2+}$, and $Ru(i\text{-biq})_3^{2+}$ (bpy = 2,2′-bipyridine, *i*-biq = 2,2′-biisoquinoline) have been studied and compared with those of the previously studied $Ru(bpy)_3^{2+}$. The electrochemical behavior of the same complexes has also been investigated. The spectroscopic results show that the *i*-biq ligand is not involved in the low-energy excited states that are responsible for the luminescence emission of the mixed-ligand complexes, and the electrochemical data show that the presence of one or two *i*-biq ligands affects only slightly the density of charge on the Ru ion compared with the situation found for $Ru(bpy)_3^{2+}$. $Ru(bpy)(i\text{-biq})_2^{2+}$ can thus be regarded as containing the $Ru(bpy)^{2+}$ emitting unit in a situation that, except for ligand–ligand interaction, is essentially the same as that experienced by such a unit in the $Ru(bpy)_2(i\text{-biq})^{2+}$ and $Ru(bpy)_3^{2+}$ complexes. The electrochemical and spectroscopic results suggest that $Ru(bpy)(i\text{-biq})_2^{2+}$, $Ru(bpy)_2(i\text{-biq})^{2+}$, and $Ru(bpy)_3^{2+}$ can all be described as containing single-bpy-localized excited states but that in the last two complexes there is a weak bpy interligand interaction.

Introduction

The photophysical properties of transition-metal complexes continue to be extensively investigated for both theoretical reasons[4-6] and potential applications in the field of energy conversion.[7-16] In particular, much attention has been devoted to the

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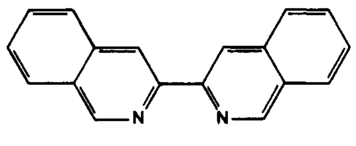
Table I. Spectroscopic and Electrochemical Properties of the Ru(bpy)$_n$(i-biq)$_{3-n}$$^{2+}$ Complexes

	absorption 293 K[b]		emission 84 K[c]		emission 293 K[b]		oxidn[a]	redn[a]		
	λ_{max}, nm	ϵ	λ_{max}, nm	τ, μs	λ_{max}, nm	τ, μs	$E_{1/2}$, V	$E_{1/2}(1)$, V	$E_{1/2}(2)$, V	$E_{1/2}(3)$, V
Ru(bpy)$_3$$^{2+}$	452	13 000	582	5.0	608	1.1	+1.26	−1.35	−1.53	−1.78
Ru(bpy)$_2$(i-biq)$^{2+}$	450 sh	11 900	586	4.7	610	1.1	+1.22	−1.38	−1.57	−1.72
Ru(bpy)(i-biq)$_2$$^{2+}$	450 sh	11 600	586	5.0	615	1.0	+1.17	−1.42	−1.64[d]	−1.74[d]
Ru(i-biq)$_3$$^{2+}$	392	24 100	540	96	543[e]	0.25[e]	+1.12	−1.51[d]	−1.76[d]	

[a] Conditions: acetonitrile solution; estimated error ±0.02 V; reversible or nearly reversible ($\Delta i_p < 80$ mV) unless otherwise noted. [b] In acetonitrile; estimated error <8%. [c] In propionitrile/butyronitrile (4:5 v/v). [d] Irreversible. [e] $T = 250$ K.



i-biq

Figure 1. Structural formula of 2,2′-biisoquinoline.

Ru(bpy)$_3$$^{2+}$ complex (bpy = 2,2′-bipyridine),[15,16] which is widely used as a light absorption sensitizer[17] in the conversion of light into chemical (or electrical) energy and as a light emission sensitizer[17] in the conversion of chemical (or electrical) energy into light. In spite of the great number of spectroscopic, electrochemical, photochemical, and theoretical studies,[18-35] questions remain concerning the detailed description of the excited states of this complex. A particularly interesting problem is whether the lowest metal-to-ligand charge-transfer (MLCT) excited states, which are responsible for the luminescence emission, are best described as multichelate ring delocalized with molecular D_3 symmetry[20] or single chelate ring localized (spatially isolated) with C_{2v} symmetry and a smaller amount of interligand interaction.[6]

Studies concerning Ru(bpy)$_n$(L)$_{3-n}$$^{2+}$ (n = 0, 1, 2) complexes[36-49] may be important not only to tune the excited-state properties in a controlled manner but also to obtain a better understanding

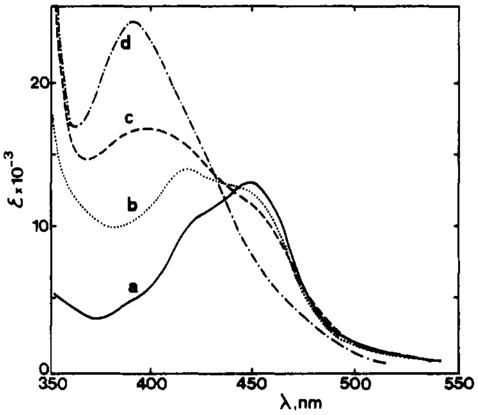


Figure 2. Absorption spectra in acetonitrile solution at room temperature of (a) Ru(bpy)$_3$$^{2+}$, (b) Ru(bpy)$_2$($i$-biq)$^{2+}$, (c) Ru(bpy)($i$-biq)$_2$$^{2+}$, and (d) Ru($i$-biq)$_3$$^{2+}$.

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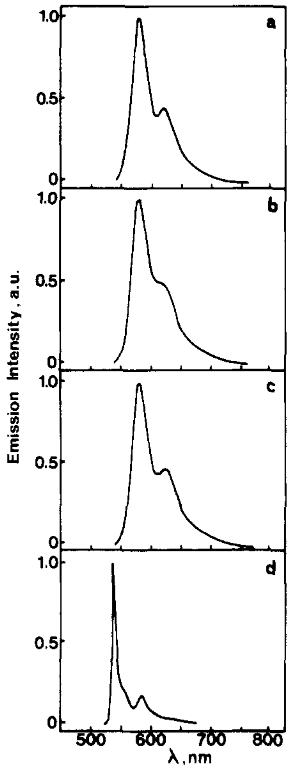

Figure 3. Emission spectra in propionitrile/butyronitrile (4:5 v/v) solution at 84 K of (a) $Ru(bpy)_3^{2+}$, (b) $Ru(bpy)_2(i\text{-biq})^{2+}$, (c) $Ru(bpy)(i\text{-biq})_2^{2+}$, and (d) $Ru(i\text{-biq})_3^{2+}$.

of the electronic situation of $Ru(bpy)_3^{2+}$ itself. From the latter point of view, the 2,2′-biisoquinoline (*i*-biq, Figure 1) ligand is very interesting because in the mixed-ligand $Ru(bpy)_n(i\text{-biq})_{3-n}^{2+}$ complexes it plays the role of spectator as far as the properties of the low-energy MLCT excited states are concerned. This has allowed us to study the behavior of the $Ru(bpy)^{2+}$ and $Ru(bpy)_2^{2+}$ emitting units and to compare their properties with those of the $Ru(bpy)_3^{2+}$ complex.

Experimental Section

$Ru(bpy)_3^{2+}$, $Ru(bpy)_2(i\text{-biq})^{2+}$, $Ru(bpy)(i\text{-biq})_2^{2+}$, and $Ru(i\text{-biq})_3^{2+}$ as PF_6^- salts were prepared as described elsewhere.[36a] Diluted solutions (10^{-5}–10^{-4} M) of each complex were sealed under vacuum in 1-cm quartz cells after repeated freeze–pump–thaw cycles. The absorption spectra were recorded with a Perkin-Elmer 323 spectrophotometer. The emission spectra were obtained with a Perkin-Elmer MPF-44B spectrofluorimeter equipped with a Hamamatsu R928 phototube. Excitation was performed in the high-intensity bands of the visible region or at 337 nm, with the same results. Excitation spectra were obtained with a Perkin-Elmer 650–40 spectrofluorimeter. The emission was monitored at 615 nm, and the spectrum was corrected for the change in emission intensity of the lamp with use of Rhodamine B as a quantum counter.[50] Emission lifetimes were measured by a modified Applied Photophysics single photon counting apparatus equipped with a nitrogen thyratron gated source lamp. The decay was monitored at the maximum of the emission band. Data treatment was carried out with a Digital PDP/11 microcomputer. Standard iterative nonlinear programs were employed to analyze the emission curves.[51] The quality of the fit was assessed by the χ^2 values close to unity and the residuals regularly distributed along the time axis. Single-exponential decays were obtained for each complex in all cases.

For the temperature-dependence experiments the solvent chosen was a propionitrile–butyronitrile (4:5 v/v) mixture because of its low freezing temperature. The samples were maintained inside a Thor C600 nitrogen-flow cryostat, equipped with a Thor 3030 temperature controller and indicator. The absolute error is estimated to be ±2 K. The relative emission intensities at the various temperatures were obtained from the area of the emission bands. Corrections for the photomultiplier response were negligible because above the glass transition temperature the position of the band maximum did not change, and the band shape changed only slightly with increasing temperature. Any temperature dependence of the refractive index was neglected. The absorbance change with temperature (due to solvent contraction) was also neglected.

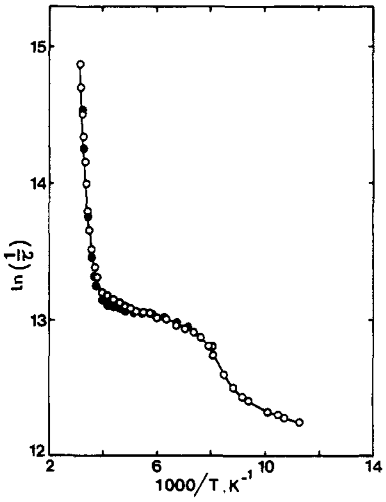

Figure 4. Temperature dependence of emission lifetime (○) and relative emission intensity (●) in propionitrile/butyronitrile (4:5 v/v) solution for $Ru(bpy)_3^{2+}$.

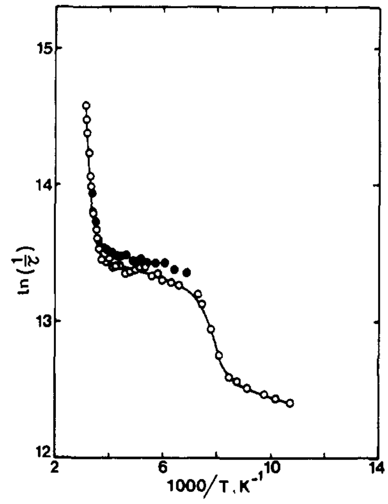

Figure 5. Temperature dependence of emission lifetime (○) and relative emission intensity (●) in propionitrile/butyronitrile (4:5 v/v) solution for $Ru(bpy)_2(i\text{-biq})^{2+}$.

Electrochemical measurements were carried out by using a Metrohm E/506 Polarecord, a Metrohm E/612 VA scanner, and a Hewlett-Packard 7044A X-Y recorder. Cyclic voltammograms were obtained in acetonitrile solutions by using a stationary platinum-disk working electrode, a platinum counterelectrode, and an Ag/0.01 M $AgNO_3$ reference electrode, with TBAP as supporting electrolyte. Scanning speed was 200 mV s^{-1}.

Results

A summary of the absorption spectra, emission spectra, emission lifetimes, and oxidation and reduction potentials are given in Table I. Figure 2 shows the absorption spectra in the visible region of the four complexes at room temperature, and Figure 3 shows the emission spectra at 84 K. The excitation spectra (not shown) of the mixed-ligand complexes were found to match the absorption spectra. Figures 4–7 show the temperature dependence of the emission lifetimes and of the relative emission intensities (as ln $(1/\phi_e) + c$, where c is an arbitrary scaling constant) for the four complexes examined. The temperature region examined included the temperature range (around 120 K) in which the solvent undergoes a change from fluid solution to rigid glass. In such a region a strong discontinuity in the plot is observed (Figures 4–7). The experimental values ln $(1/\tau)$ vs. $1/T$ were fitted by a two-expo-

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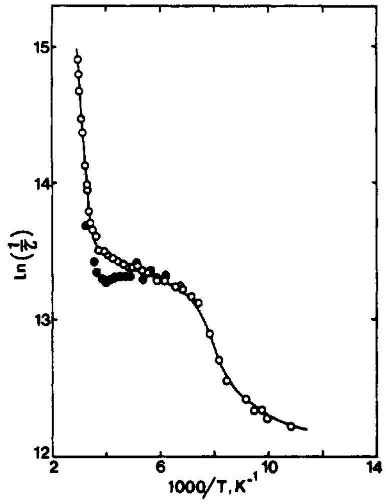

Figure 6. Temperature dependence of emission lifetime (○) and relative emission intensity (●) in propionitrile/butyronitrile (4:5 v/v) solution for $Ru(bpy)(\textit{i}\text{-}biq)_2^{2+}$.

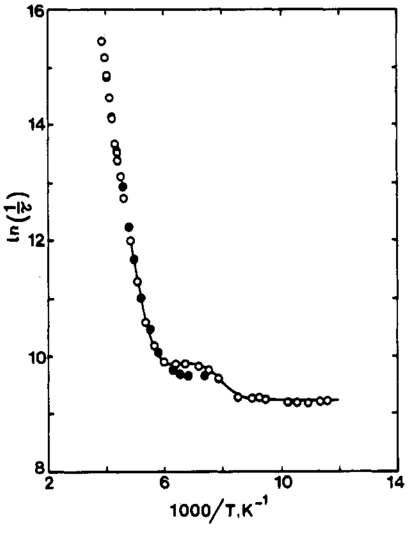

Figure 7. Temperature dependence of emission lifetime (○) and relative emission intensity (●) in propionitrile/butyronitrile (4:5 v/v) solution for $Ru(\textit{i}\text{-}biq)_3^{2+}$.

nential expression employing an iterative nonlinear procedure.[51] Quite similar values were obtained for the various parameters by fitting either the data above the melting temperature of the solvent by eq 1 or the full temperature range by a modified form of eq

$$1/\tau = k_0 + A_1 e^{-\Delta E_1/RT} + A_2 e^{-\Delta E_2/RT} \qquad (1)$$

1 that takes into account the discontinuity due to the melting of the solvent.[36d] In eq 1 k_0 stands for the low-temperature limiting value, A_1 and A_2 are frequency factors, and ΔE_1 and ΔE_2 are activation barriers. The values of the various parameters extracted by the fitting procedure are reported in Table II.

Discussion

Spectroscopic and Redox Properties. The bands shown by $Ru(bpy)_3^{2+}$[20] and $Ru(\textit{i}\text{-}biq)_3^{2+}$[52] in the visible region (Figure 2) are due to metal-to-ligand charge-transfer (MLCT) transitions. Note that the MLCT bands of $Ru(\textit{i}\text{-}biq)_3^{2+}$ are blue shifted compared to those of $Ru(bpy)_3^{2+}$. One can see (Figure 2) that the mixed-ligand complexes exhibit both Ru → bpy and Ru → *i*-biq CT bands.

It is well-known that the $Ru(bpy)_3^{2+}$ luminescence has MLCT orbital origin and, formally, triplet multiplicity.[15,16] By contrast, the $Ru(\textit{i}\text{-}biq)_3^{2+}$ emission is a ligand-centered phosphorescence.[52] The lowest ^{3}MLCT excited state of $Ru(\textit{i}\text{-}biq)_3^{2+}$ is estimated to lie at 20 500 cm^{-1},[52] in agreement with the blue shift of the corresponding absorption bands. As one can see from Figure 3 and Table I, the mixed-ligand complexes exhibit only one emission band,[53] which has practically the same λ_{max} and τ as the $Ru(bpy)_3^{2+}$ emission. This shows that the emitting excited states of the mixed-ligand complexes are essentially Ru → bpy CT in nature. The matching between absorption and excitation spectra shows that the emitting excited state is populated with the same efficiency from excited states involving either bpy or *i*-biq. Thus, the spectroscopic results show that in the mixed-ligand complexes the coupling between excited states involving bpy and excited states involving *i*-biq is too weak to affect the energy levels in a substantial way but strong enough to allow fast radiationless deactivation of the upper excited states to the lowest one.

The reduction potentials of the free bpy and *i*-biq ligands are almost equal (−2.22 and −2.20 V, respectively[52]). The reduction potential of $Ru(bpy)_3^{2+}$, which is known to correspond to the reduction of one bpy ligand,[6] is less negative than that of $Ru(\textit{i}\text{-}biq)_3^{2+}$ (Table I). This shows that, once coordinated to Ru^{2+}, *i*-biq becomes a worse π acceptor than bpy. In other words, the π^*_L LUMO orbital lies at higher energy in *i*-biq than in bpy, as is also indicated by the spectroscopic results. This different behavior cannot be due to a difference in the σ-donor properties of *i*-biq compared to those of bpy, because both have the same pK_a values.[54] It is probably due to a smaller localization of the π^* orbitals on nitrogen in *i*-biq.[57] On the other hand, the more positive oxidation potential of $Ru(bpy)_3^{2+}$ compared with that of $Ru(\textit{i}\text{-}biq)_3^{2+}$ shows that the π_M HOMO is slightly lower in the former complex, as a result of the better π-acceptor properties of bpy.

As far as the mixed-ligand complexes are concerned, Table I shows that the first reduction potential decreases very little and smoothly on replacing one or two bpy ligands by *i*-biq, while the potential becomes considerably more negative (and irreversible) when the third bpy ligand is replaced. This shows that in the mixed-ligand complexes the first reduction process involves bpy. The small shift toward more negative potentials is in agreement with the weaker π-acceptor properties of *i*-biq. The oxidation potential also varies very little and smoothly on replacing bpy by *i*-biq (Table I). This suggests[44,45a,58-60] that the effective nuclear charge on the metal decreases only very slightly when bpy is replaced by *i*-biq. The difference between the $Ru^{3+/2+}$ potential and the first reduction potential, which is a measure of the difference in energy between HOMO and LUMO of the Ru(II) complexes,[45a] is practically constant for the three complexes containing bpy, in agreement with the practically constant values of the emission energies.

In conclusion, (i) the spectroscopic data show that the *i*-biq ligand is not involved in the low-energy excited states that are

Table II. Parameters Obtained by Temperature-Dependent τ Measurements (See Eq 1)[a]

	A_1, s^{-1}	ΔE_1, cm^{-1}	A_2, s^{-1}	ΔE_2, cm^{-1}	k_0, s^{-1}
$Ru(\textit{i}\text{-}biq)_3^{2+}$	1.0×10^{13}	2580			1.9×10^4
$Ru(bpy)(\textit{i}\text{-}biq)_2^{2+}$	4.3×10^{13}	3890	7.8×10^5	110	2.9×10^5
$Ru(bpy)_2(\textit{i}\text{-}biq)^{2+}$	4.9×10^{13}	3850	4.8×10^5	65	3.1×10^5
$Ru(bpy)_3^{2+}$	1.3×10^{14}	3960	5.6×10^5	90	2.4×10^5

[a] Estimated errors on ΔE_2 ~20% and on ΔE_1 ≤10%; solvent propionitrile/butyronitrile (4:5 v/v).

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(53) No example of bona fide dual emission has been reported for Ru(II) chelates.[36e]

(54) pK_a values of *i*-biq and bpy, measured in 75% EtOH/25% H_2O (v/v), are the same (3.9) within experimental uncertainity.[55,56]

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responsible for the luminescence emission of the mixed-ligand complexes and (ii) the electrochemical data show that the presence of one or two *i*-biq ligands affects only slightly the density of charge on the Ru ion compared with the situation found for Ru(bpy)$_3^{2+}$. Thus, Ru(bpy)(*i*-biq)$_2^{2+}$ can be regarded as containing the Ru(bpy)$^{2+}$ emitting unit in a situation that, except for ligand–ligand interactions, is essentially the same as that experienced by such a unit in the Ru(bpy)$_2$(*i*-biq)$^{2+}$ and Ru(bpy)$_3^{2+}$ complexes.

Temperature Dependence of the Luminescence Lifetime. The analysis of the temperature dependence of the emission lifetime (Table II) has shown that the three complexes containing bpy exhibit a quite similar energy level situation. There are two closely spaced, thermally equilibrated levels (ΔE of the order of 10^2 cm^{-1}) that have similar decay properties (compare the values of the k_0 and A_2 parameters in Table II) and a level lying about 4000 cm^{-1} above that undergoes an efficient radiationless deactivation. For Ru(bpy)$_3^{2+}$,[61] there is a general agreement to assign (i) the low-energy closely spaced levels to MLCT states (although there is no agreement on a more detailed description of these states) and (ii) the level lying about 4000 cm^{-1} above to the lowest triplet metal-centered (^{3}MC) excited state responsible for the photoracemization[63] and photosubstitution[30a,62] reactions. In view of the strict similarity of the experimental behavior, it seems quite reasonable to extend the same assignments to the levels found for the mixed-ligand complexes. This is also supported by the following considerations based on the spectroscopic and electrochemical results discussed above: (a) the *i*-biq ligand is not involved in the low-energy excited states that are responsible for the luminescence emission; (b) the ^{3}LC excited state of *i*-biq, which lies about 1300 cm^{-1} above the emitting Ru → bpy CT excited state,[52] does not undergo fast deactivation (see the k_0 value of Ru(*i*-biq)$_3^{2+}$, Table II), and thus its population on increasing temperature does not affect the emission lifetime; (c) the lowest ^{3}MC excited state is expected to lie at about the same energy as in Ru(bpy)$_3^{2+}$ since bpy and *i*-biq should have similar ligand field strength.[52]

Thus, the Ru(bpy)(*i*-biq)$_2^{2+}$, Ru(bpy)$_2$(*i*-biq)$^{2+}$, and Ru(bpy)$_3^{2+}$ complexes behave quite similarly from an experimental point of view and their behavior must be described on the basis of energy levels of the same orbital origin (i.e., Ru → bpy CT, and MC). This conclusion suggests that the emitting unit is in all cases the Ru(bpy)$^{2+}$ unit, in agreement with the single-bpy-localized model[19a] recently invoked by several authors to interpret spectroscopic and electrochemical results concerning Ru(bpy)$_3^{2+}$.[19,21,22,24b,25,27,30,31,32b]

As far as Ru(*i*-biq)$_3^{2+}$ is concerned, the temperature dependence of the luminescence lifetime (Figure 7, Table II) shows that a level lying about 2600 cm^{-1} above the ^{3}LC emitting level is responsible for a fast radiationless deactivation. Since the ^{3}LC level lies at 18 500 cm^{-1}, the upper level should lie at about 21 000 cm^{-1}, i.e. approximately at the same energy as the ^{3}MC excited state of Ru(bpy)$_3^{2+}$ and of the mixed-ligand complexes (see above). This suggests that the level responsible for the fast radiationless deactivation of Ru(*i*-biq)$_3^{2+}$ is again the lowest ^{3}MC excited state.

Temperature Dependence of the Luminescence Emission. As one can see from Figure 6, the emission lifetime of Ru(bpy)(*i*-biq)$_2^{2+}$ *decreases* with increasing temperature in all the temperature range examined, whereas the emission intensity *increases* with increasing temperature in the 150–250 K range. This shows that the decrease in the emission lifetime of the level that lies 110 cm^{-1} above the lowest one is due to a larger radiative rate constant. We suggest the following symmetry-based explanation, neglecting solvent effects. Under the C_{2v} symmetry of the Ru(bpy)$^{2+}$ unit[64] the $\pi_M(t_{2g})$ octahedral orbitals split into a_1, b_1, and b_2, and the $\pi^*(\psi)$ bpy orbital[28,65] belongs to the b_1 symmetry. From the overlap between the b_1 metal and ligand orbitals, first-order bonding and antibonding orbitals are obtained. The low-energy MLCT excited states, which are obtained by promoting an electron from the b_1 bonding and a_1 and b_2 nonbonding (metal) orbitals to the b_1 antibonding (ligand) orbital, have A_1, B_1, and A_2 symmetry and triplet multiplicity. The $^3A_1$ state, deriving from the transition between bonding and antibonding orbitals, lies at higher energies than the $^3B_1$ and $^3A_2$ states. Spin–orbit coupling splits each state as follows:[66] $^3A_1$ to A_2, B_1, B_2; $^3B_1$ to A_1, A_2, B_2; $^3A_2$ to B_1, B_2, A_1. The $A_2 \rightarrow A_1$ transition is forbidden, the $B_1 \rightarrow A_1$ transition is allowed along the x axis, the $B_2 \rightarrow A_1$ transition is y allowed, and the $A_1 \rightarrow A_1$ transition is z allowed. Since the main transition moment of the MLCT excitation lies along the z axis,[65] the radiative rate constant of the z-allowed transition is expected to be much larger than those of the other transitions. Thus, in both the $^3B_1$ and $^3A_2$ manifolds (one of which has to be the lowest energy one) there is a level that can exhibit a larger radiative rate constant than the others through spin–orbit mixing with the z-allowed $^1A_1 \rightarrow {}^1A_1$ transition. If such a level is not the lowest energy one in its manifold, it can be expected that its population on increasing temperature will cause a *decrease* in the emission lifetime and an *increase* in the emission intensity as is experimentally observed (Figure 6). An alternative mechanism that could explain the inverted behavior of emission intensity and emission lifetime is vibronic mixing. In the considered C_{2v} symmetry, low-lying spin–orbit states of A_2, B_1, and B_2 symmetry could borrow intensity from the $^1A_1$ state through the activity of low-frequency vibrations of appropriate symmetry.[67] This would in fact appear as an activated path that leads from a low-lying level to a higher one having larger radiative constant.

As one can see from Figures 4 and 5, the temperature dependence of the luminescence intensity of Ru(bpy)$_3^{2+}$ and Ru(bpy)$_2$(*i*-biq)$^{2+}$ in the 150–250 K range shows a different behavior compared with that discussed above for Ru(bpy)(*i*-biq)$_2^{2+}$ (Figure 6). This shows that there is some interligand interaction that affects slightly the energy of the various levels but may have stronger consequences on the radiative rate constants. Such an interaction can presumably be described as a weak exciton coupling[6,68] among the spin–orbit (or spin–orbit–vibronic) levels of the single Ru(bpy)$^{2+}$ units.

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Registry No. Ru(bpy)$_3^{2+}$, 15158-62-0; Ru(bpy)$_2$(*i*-biq)$^{2+}$, 89340-69-2; Ru(bpy)(*i*-biq)$_2^{2+}$, 89340-69-2; Ru(*i*-biq)$_3^{2+}$, 82762-29-6.

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(61) The temperature dependence of the luminescence emission of Ru(bpy)$_3^{2+}$ had previously been studied by several authors in different temperature ranges and/or different solvents.[5,20,30,62] The present results are consistent with those previously reported.

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