

atively charged reactants and a foreign cation; namely, the role of the cation is to reduce the Coulombic barrier of the two reactants in order to form an encounter complex.³⁻⁵ Alternatively, the correlation with the polarizability was taken as evidence for the electron-mediating role of the cation between reductant and oxidant.³ Figure 1 shows the plot of the quenching rate constant of the present reaction against the Stokes radii of the cations. Linear correlation was observed except for the case of the $(C_2H_5)_4N^+$ ion. The present quenching rate constant displays good linear correlation with the thermal electron-self-exchange rate constants of $[Fe(CN)_6]^{3-/4-}$ ¹⁸ and $MnO_4^{2-/5-}$ and the oxidation rate of $[Mo(CN)_8]^{4-}$ with $S_2O_8^{2-}$ for various alkali-metal ions, which indicates that alkali-metal ions play a similar role for both the photoquenching and the thermal electron-transfer reactions over the wide range of rate constants. The exceptional behavior of $(C_2H_5)_4N^+$ in the plot of Figure 1 may be related to the ob-

servation of the spectral change of the reactants in the presence of the cation (vide supra).

In conclusion, the cation effect seems to provide strong evidence that the photoquenching reaction proceeds through an encounter complex that is an ion triplet containing the foreign cation, which reduces the Coulombic barrier. A long-distance electron- or energy-transfer mechanism is clearly ruled out. The present results indicate that any quantitative treatment of photoquenching rate constants should take electrolyte effect into consideration, particularly for reactants with the same charge sign.

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Mononuclear, Dinuclear, and Trinuclear Ruthenium(II) Complexes of a Tris(bipyridine) Bridging Ligand: Syntheses, Absorption Spectra, Redox Potentials, and Photophysical Properties

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The tris(bipyridine) ligand **1**, 1,3,5-tris[(((5-(ethoxycarbonyl)-2,2'-bipyridyl-5'-yl)carbonyl)benzylamino)methyl]benzene, previously used to prepare a hemicaged Ru(II) complex, $1[Ru]^{2+}$, has now been employed as a ligand capable of coordinating one, two, or three $Ru(bpy)_2^{2+}$ units. The three new complexes $1[Ru(bpy)_2]^{2+}$, $1[Ru(bpy)_2]_2^{4+}$, and $1[Ru(bpy)_2]_3^{6+}$ have been synthesized as PF_6^- salts, and their spectroscopic and electrochemical properties have been investigated. The absorption spectra of the complexes exhibit bpy and **1** ligand-centered bands in the UV region and $Ru \rightarrow bpy$ and $Ru \rightarrow 1$ charge-transfer bands in the visible region, with the latter being at lower energy. In acetonitrile solution, all the complexes exhibit a reversible oxidation wave, centered on the metal, at +1.36 V and a reversible reduction wave, centered on the coordinated bpy-type arm of **1**, at -0.91 V vs SCE. Other reduction waves are present at more negative potentials. All the waves are mono-electronic, dielectronic, and trielectronic for the mononuclear, dinuclear, and trinuclear complexes, respectively. The luminescence properties are the same for the three complexes, with a band at 654 nm ($\tau \sim 1.4 \mu s$) in a propionitrile-butyronitrile rigid matrix at 77 K and a band at 700 nm ($\tau = 60$ ns) in a fluid propionitrile-butyronitrile solution at room temperature, indicating that (i) the lowest MLCT excited state involves the bpy-type coordinated arm of **1** in each complex and (ii) there is no strong interaction between the metal-containing chromophoric units. However, the fluorescence of the bpy-type arms of **1**, observable in the free ligand **1** at 77 K, is no longer present in $1[Ru(bpy)_2]^{2+}$, indicating the occurrence of an intramolecular quenching. Excitation spectra performed on $1[Ru(bpy)_2]^{2+}$ confirm that there is an efficient mechanism for intramolecular energy transfer from the two noncoordinated arms of **1** and the metal-containing chromophoric unit.

Introduction

Mononuclear Ru(II)-polypyridine complexes are highly luminescent species and powerful reactants for light-induced and light-generating electron-transfer processes.² For a variety of practical applications, however, *multicenter* luminescent and redox systems are expected to be more useful.³ The synthesis and characterization of polynuclear coordination compounds having

desired photophysical and electrochemical properties is currently an important research field, and a great number of papers have recently appeared on this subject.⁴⁻²³

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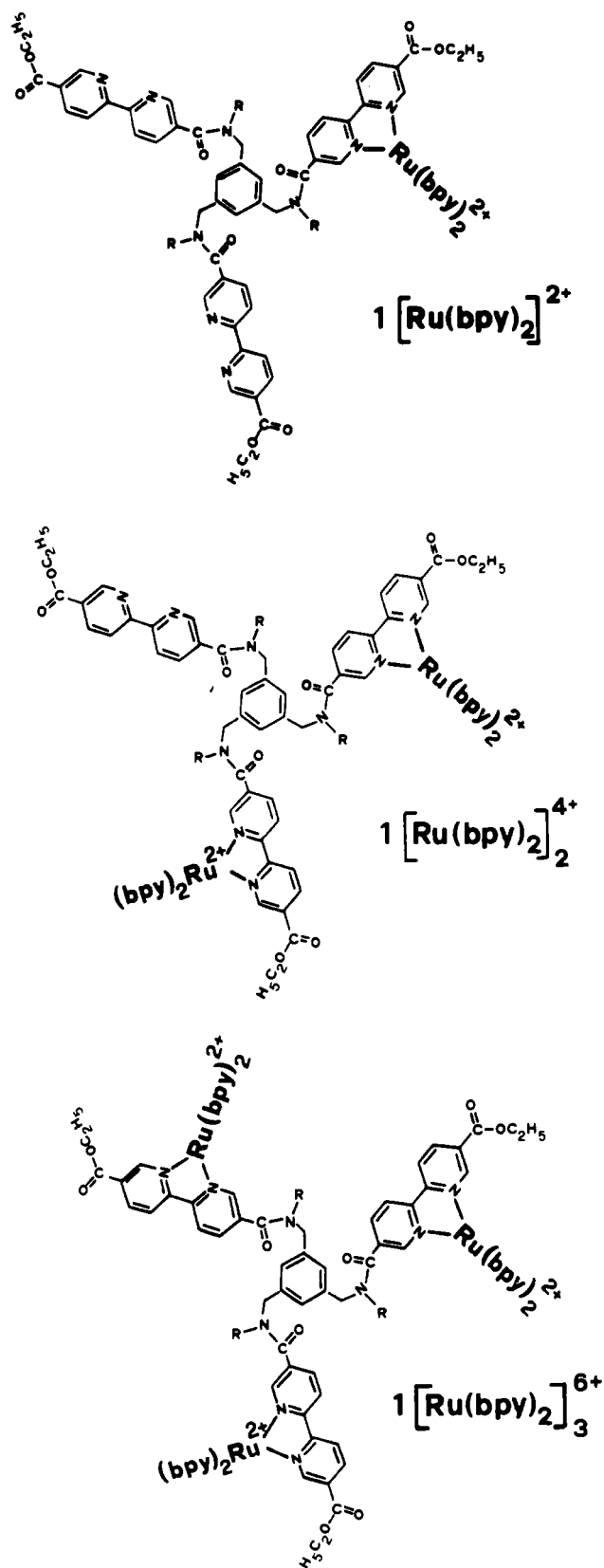


Figure 1. Structures of the mono-, di-, and trinuclear ruthenium complexes.

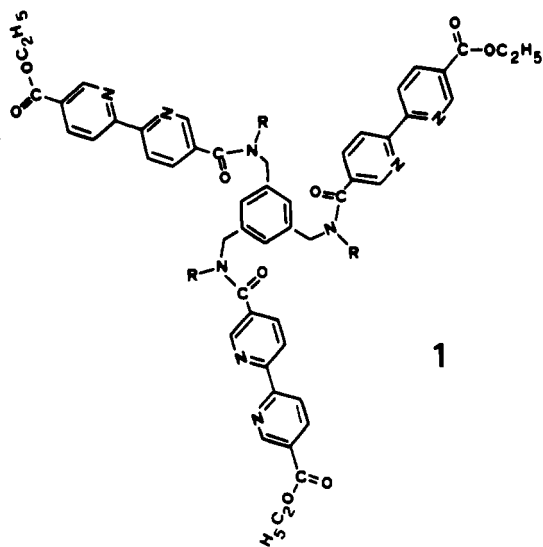
Key components of polynuclear coordination compounds are the bridging ligand and the metal-containing building blocks. The

knowledge accumulated in the last 15 years on mononuclear complexes provides some guidelines for the choice of these components.^{2,24,25} For example, combination of polypyridine-type bridging ligands and Ru(II)-polypyridine building blocks is certainly an appropriate way for the design of luminescent and redox-active polynuclear complexes.

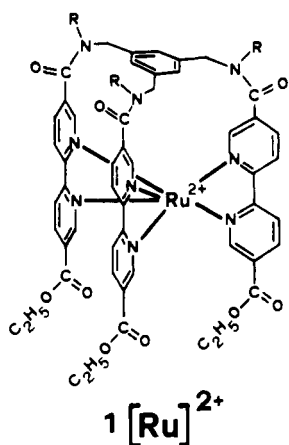
The tris(bipyridine) ligand **1**, 1,3,5-tris[(((5-(ethoxycarbonyl)-2,2'-bipyridyl-5'-yl)carbonyl)benzylamino)methyl]-benzene, previously used to prepare hemicaged Fe(II),²⁶ Rh(III),²⁷ and Ru(II)^{28,29} complexes, can also be employed as a bridging

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ligand capable of coordinating one, two, or three metal-containing building blocks. Our final aim is to obtain supramolecular systems based on the tripod ligand **1** and on three different (in excited-state energy and/or redox potential) luminescent and redox-active units. As a first step in this direction we have synthesized and characterized the mononuclear $1[\text{Ru}(\text{bpy})_2]^{2+}$, dinuclear $1[\text{Ru}(\text{bpy})_2]_2^{4+}$, and trinuclear $1[\text{Ru}(\text{bpy})_2]_3^{6+}$ complexes of **1** with $\text{Ru}(\text{bpy})_2^{2+}$ units (see Figure 1). We report here the absorption spectra, redox potentials, and photophysical properties of these three new complexes, and we compare the results obtained with those previously available for $\text{Ru}(\text{bpy})_3^{2+}$ and the hemicaged $\text{Ru}(\text{II})$ complex of **1**²⁹ (the latter will hereafter be designated by $1[\text{Ru}]^{2+}$).



Experimental Section

The tripod ligand **1** was prepared as previously described.^{26,27} The preparative procedure for $1[\text{Ru}(\text{bpy})_2](\text{PF}_6)_2$ involved substitution of chloride ions in the coordination sphere of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ by one bpy unit of the bridging ligand **1**. This was achieved by reacting $\text{Ru}(\text{bpy})_2\text{Cl}_2$ (0.1 mM) with an excess of **1** (1.0 mM) in ethylene glycol (10% water) for 3 h at 120 °C. The formation of the monomeric species was followed by thin-layer chromatography during the reaction time, and the product was isolated by distilling off the solvent, dissolving the residue in H_2O , and precipitating the compound by addition of a saturated aqueous solution of NH_4PF_6 . The precipitate was filtered off, washed with water, and redissolved in the minimum volume of acetonitrile. The complex was then purified by column chromatography (silica gel) using 1:1 ethanol- H_2O (containing 10% NaCl) as an eluent. The first orange fraction, containing only the monomeric species, was collected and evaporated to dryness. The residue was washed several times with H_2O to eliminate NaCl and redissolved in acetonitrile. Addition of ether caused the pre-

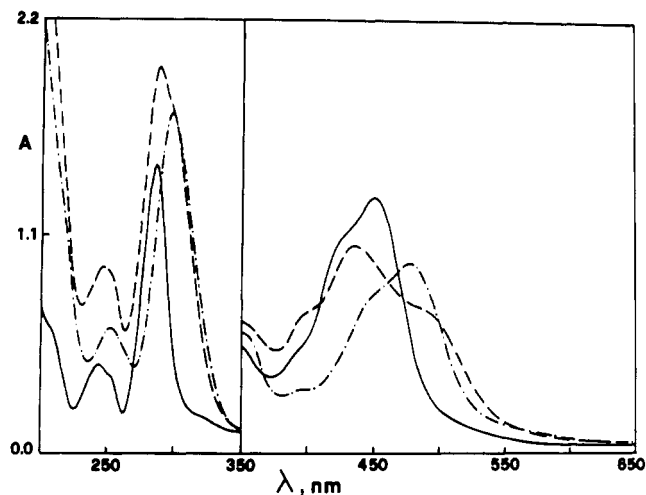


Figure 2. Absorption spectra of 1.9×10^{-5} M $1[\text{Ru}(\text{bpy})_2]^{2+}$ (---), $1[\text{Ru}]^{2+}$ (-·-), and $\text{Ru}(\text{bpy})_3^{2+}$ (—) in acetonitrile at room temperature. The absorbance scale for the 350–650-nm region has been expanded by a factor of 5.

cipitation of the compound. The pure mononuclear complex was dried and characterized (yield 70%). The dinuclear $1[\text{Ru}(\text{bpy})_2]_2(\text{PF}_6)_4$ complex was synthesized in an analogous manner, except the reactants were mixed in stoichiometric amounts and were allowed to react for 5 h. The compound was purified by silica gel chromatography and recrystallized from acetonitrile ether (yield 55%). The trinuclear $1[\text{Ru}(\text{bpy})_2]_3(\text{PF}_6)_6$ complex was prepared by using an excess of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ and prolonging the reaction time for 10 h (yield 75%). Because of its high charge, the complex did not exhibit any tendency to move on the chromatographic column, and therefore a DMF- H_2O (containing 5% NH_4Cl) 1:1 mixture was used as an eluent.

All complexes were characterized by elemental analysis and ^1H NMR and IR spectroscopy. Elemental analysis gave satisfactory results, if the inclusion of solvent molecules is taken into account. ^1H NMR spectra are rather complex in the "aromatic" region, but the signals of the ester groups of coordinating arms and those of the free bpy groups can clearly be distinguished. Their relative intensities agree with the expected values. A FAB-MS spectrum was obtained for the complex $1[\text{Ru}(\text{bpy})_2](\text{PF}_6)_2$, showing $M^+ - \text{PF}_6$ (m/e 1757) and $M^+ - 2(\text{PF}_6)$ (m/e 1611) masses. FAB-MS spectra were not accessible for $1[\text{Ru}(\text{bpy})_2]_2(\text{PF}_6)_4$ and $1[\text{Ru}(\text{bpy})_2]_3(\text{PF}_6)_6$ due to the high molecular mass. The absorption spectra, emission spectra, emission quantum yields, emission lifetimes, and electrochemical potentials were obtained as previously described.²⁹

Results and Discussion

$1[\text{Ru}(\text{bpy})_2]^{2+}$, $1[\text{Ru}(\text{bpy})_2]_2^{4+}$, and $1[\text{Ru}(\text{bpy})_2]_3^{6+}$ are interesting for two reasons: (i) they are mixed-ligand complexes, and thus one can compare their spectroscopic, photophysical, and electrochemical properties with those of the parent homoleptic $\text{Ru}(\text{bpy})_3^{2+}$ and $1[\text{Ru}]^{2+}$ complexes; (ii) they constitute a family of mononuclear, dinuclear, and trinuclear complexes of a tripod bridging ligand, so that one can study the interactions occurring among the various chromophoric or redox units that are present in each complex.

Absorption Spectra. The absorption spectra of $1[\text{Ru}(\text{bpy})_2]^{2+}$ (Figure 2), $1[\text{Ru}(\text{bpy})_2]_2^{4+}$, and $1[\text{Ru}(\text{bpy})_2]_3^{6+}$ are characterized by several intense bands in the UV and visible regions. Comparison with the spectra of the free ligands bpy and **1** and of the parent $\text{Ru}(\text{bpy})_3^{2+}$ and $1[\text{Ru}]^{2+}$ complexes (Table I) shows that the bands around 250 and 300 nm result from ligand-centered (LC) transitions and those in the visible region are due to metal-to-ligand charge-transfer (MLCT) transitions. The bpy-type arms of the tripod ligand have properties slightly different from those of bpy because of the presence of electron-withdrawing ester and amido groups. Both in the free ligands and in their homoleptic complexes $1[\text{Ru}]^{2+}$ and $\text{Ru}(\text{bpy})_3^{2+}$, the LC bands of **1** are slightly displaced to the red region compared to the LC bands of bpy. The two types of LC bands overlap in the mixed-ligand complexes, as one can clearly see from Figure 2: the spectrum of $1[\text{Ru}(\text{bpy})_2]^{2+}$ shows a maximum at 290 nm, very close to the maxima exhibited by $\text{Ru}(\text{bpy})_3^{2+}$ (288 nm) and $1[\text{Ru}]^{2+}$ (298 nm). It should also be noted that the maximum of the band of **1** coincides

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Table I. Spectroscopic and Photophysical Properties

	absorption ^a (298 K) λ_{\max} , nm (ϵ , M ⁻¹ cm ⁻¹)	emission ^b				
		77 K		298 K		
		λ_{\max} , nm	τ , ^c μ s	λ_{\max} , nm	τ , ^c μ s	$10^2\Phi$
$1[\text{Ru}(\text{bpy})_2]^{2+}$	290 (112 000), 400 (sh), 436 (11 500), 488 (sh)	654	1.6	700	0.060	0.37
$1[\text{Ru}(\text{bpy})_2]_2^{4+}$	288 (175 000), 400 (sh), 436 (22 900), 488 (sh)	654	1.3	702	0.060	0.36
$1[\text{Ru}(\text{bpy})_2]_3^{6+}$	287 (243 000), 400 (sh), 436 (31 000), 489 (sh)	654	1.3	702	0.060	0.32
$1[\text{Ru}]^{2+}$	298 (90 600), 478 (10 500)	620	1.9	640	0.27	1.7
$\text{Ru}(\text{bpy})_3^{2+}$	288 (76 600), 452 (13 600)	582	4.8	615	0.17	1.4
1	298 (77 000)	452, ^d 492 ^e	<i>f</i>			
bpy ^g	280 (16 300)	425 ^e	10 ⁶			

^a Acetonitrile solution. ^b Aerated propionitrile–butyronitrile solution. ^c Experimental uncertainty < 8%. ^d Fluorescence. ^e Phosphorescence. ^f See text. ^g De Armond, M. K.; Hillis, J. E. *J. Chem. Phys.* **1971**, *54*, 2247.

with the maximum of the LC bands of $1[\text{Ru}]^{2+}$ and that the extinction coefficients of the two bands are quite comparable.

In the visible region $1[\text{Ru}(\text{bpy})_2]^{2+}$ (Figure 2), $1[\text{Ru}(\text{bpy})_2]_2^{4+}$, and $1[\text{Ru}(\text{bpy})_2]_3^{6+}$ (Table I) show again a composite absorption with a maximum at 436 nm and pronounced shoulders at about 400 and 490 nm. The band maximum at 436 nm can be attributed to Ru \rightarrow bpy CT transitions. The blue shift compared with the band of the same nature in $\text{Ru}(\text{bpy})_3^{2+}$ ($\lambda_{\max} = 452$ nm) is explained by the fact that the coordinated arm of **1** is more electron withdrawing than bpy,²⁹ and this leaves more positive charge on the metal with a consequent increase in the energy of the Ru \rightarrow bpy CT transition. For the same reason, the (bpy)₂Ru \rightarrow **1** CT transition is expected to move toward lower energy compared with the Ru \rightarrow **1** CT transition of $1[\text{Ru}]^{2+}$, and it can thus be identified with the shoulder at about 490 nm. The shoulder at about 400 nm roughly corresponds to that present in the $\text{Ru}(\text{bpy})_3^{2+}$ spectrum, blue shifted as for the absorption maximum.

Luminescence. $1[\text{Ru}(\text{bpy})_2]^{2+}$, $1[\text{Ru}(\text{bpy})_2]_2^{4+}$, and $1[\text{Ru}(\text{bpy})_2]_3^{6+}$ are luminescent both in rigid matrix at 77 K and in fluid solution at room temperature (Table I). Their luminescence bands are quite similar in shape to the luminescence bands of the parent $\text{Ru}(\text{bpy})_3^{2+}$ and $1[\text{Ru}]^{2+}$ complexes, lie in the same energy region, and decay in the same time scale (Table I). Their luminescent excited state can thus be assigned as a triplet metal-to-ligand charge-transfer (³MLCT) level. It is also evident that the ligands involved in such a CT luminescent level are the coordinated bpy-type arms of **1**. The luminescence band of the mixed-ligand complexes, in fact, is red shifted with respect to the luminescence bands of both $\text{Ru}(\text{bpy})_3^{2+}$ and $1[\text{Ru}]^{2+}$ (Table I), as expected for the reason illustrated above when the CT absorption bands were discussed.

The slightly shorter excited-state lifetimes of the mixed-ligand complexes in rigid matrix at 77 K compared to those of the parent complexes (Table I) can be rationalized on the basis of the energy gap rule.^{24,30–32} At room temperature, both the luminescence lifetime and the luminescence quantum yield are considerably smaller for the mixed-ligand complexes. In particular, the decrease in lifetime by a factor of 20 going from 77 to 300 K contrasts sharply with the relatively small temperature dependence found for the hemicaged complex $1[\text{Ru}]^{2+}$.^{29b} This different behavior can be at least in part attributed to the much larger red shift of the luminescence band of the mixed-ligand complexes (i.e., to the much larger decrease in the energy of the luminescent level, with consequent increase in the rate of the radiationless transitions) on melting of the solvent matrix.³³ This effect should be related to a larger change in the dipole moment caused by excitation in the mixed-ligand complexes. A very common deactivation channel for the luminescent excited states of Ru(II)–polypyridine complexes is an activated radiationless transition to an upper lying, distorted, short-lived, metal-centered excited state.^{2,32,34–37} A

Table II. Electrochemical Data

	redox potentials, V ^a			
	oxdn	redn		
$1[\text{Ru}(\text{bpy})_2]^{2+}$	+1.36	-0.92	-1.31	-1.59
$1[\text{Ru}(\text{bpy})_2]_2^{4+}$	+1.36	-0.91	i	i
$1[\text{Ru}(\text{bpy})_2]_3^{6+}$	+1.35	-0.90	i	i
$1[\text{Ru}]^{2+}$	+1.54	-0.86	-0.99	-1.17
$\text{Ru}(\text{bpy})_3^{2+}$	+1.26	-1.35	-1.54	-1.79

^a Acetonitrile solution, vs SCE, room temperature. The processes are reversible unless otherwise stated (i).

temperature-dependent study, however, has shown that such an excited state is not accessible at room temperature for $1[\text{Ru}]^{2+}$.^{29b} The energy separation between the luminescent level and the upper lying metal-centered excited state is expected to be even larger in the mixed-ligand complexes than in $1[\text{Ru}]^{2+}$ because in the former the luminescent level lies at lower energy. Therefore, it seems likely that such a decay channel plays no role in determining the excited-state lifetime of the mixed-ligand complexes.

Intramolecular Energy Transfer. The free tripod ligand **1** in acetonitrile solution at room temperature shows an intense absorption band with $\lambda_{\max} = 298$ nm and no luminescence. In rigid matrix at 77 K, however, an intense unstructured fluorescence band is present with $\lambda_{\max} = 452$ nm ($\tau < 10$ ns), and a relatively intense phosphorescence with $\lambda_{\max} = 492$ nm ($\tau > 0.1$ s) can also be observed. In the homoleptic $1[\text{Ru}]^{2+}$ complex, no LC emission is observed and the corrected excitation spectrum shows that excitation in the LC bands leads to population of the luminescent ³MLCT level with practically unit efficiency. A similar behavior is of course expected (and found) for the trinuclear $1[\text{Ru}(\text{bpy})_2]_3^{6+}$ complex where each bpy-type arm of **1** is coordinated to a metal ion. For the dinuclear $1[\text{Ru}(\text{bpy})_2]_2^{4+}$ and mononuclear $1[\text{Ru}(\text{bpy})_2]^{2+}$ complexes, one and two bpy-type arms of **1**, respectively, are free from coordination and, in principle, they could give rise to LC emission. In fact, no evidence of LC luminescence has been found in $1[\text{Ru}(\text{bpy})_2]^{2+}$. Furthermore, a corrected excitation spectrum of $1[\text{Ru}(\text{bpy})_2]^{2+}$ (acetonitrile solution, room temperature) reproduces the absorption spectrum within the experimental uncertainty ($\pm 15\%$) and the quantitative comparison between the luminescence intensity at 700 nm of solutions of $1[\text{Ru}(\text{bpy})_2]^{2+}$ and $1[\text{Ru}(\text{bpy})_2]_3^{6+}$ exhibiting equal absorbance across the 280–310-nm excitation region show that excitation in the noncoordinated arms of **1** results in the population (with efficiency not far from unity) of the luminescent ³MLCT level, which involves the Ru center. The spectral overlap between the fluorescence of **1** and the MLCT absorption of $1[\text{Ru}(\text{bpy})_2]^{2+}$ is in fact excellent, so that energy transfer from noncoordinated arms to singlet MLCT levels should be very fast. Since the conformation of **1** in $1[\text{Ru}(\text{bpy})_2]^{2+}$ is not known, any speculation concerning the en-

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ergy-transfer mechanism seems inappropriate.

Electrochemistry. In the potential window examined, all the complexes exhibit an almost reversible oxidation wave and three almost reversible reduction waves. The potential values are reported in Table II, where the corresponding values previously found for $\text{Ru}(\text{bpy})_3^{2+}$ and $1[\text{Ru}]^{2+}$ are also shown. Comparison of the current intensities of the voltammograms of the three complexes (mono-, di-, and trinuclear) with the 2+/3+ oxidation wave of $\text{Ru}(5,5'\text{-Me}_2\text{-}2,2'\text{-bpy})_3^{2+}$ (+1.16 V) as internal standard indicated mono-electronic, dielectronic, and trielectronic waves, respectively. Since the oxidation potential is the same for the three mixed-ligand complexes, the interaction between the Ru centers must be very small. The difference between the formal potentials for the first and last pair of oxidation states in a molecule with n identical noninteracting redox centers follows simple statistics and is given by $(2RT/F) \ln n$.³⁸ Thus, differences of 0.035 and 0.056 V would be expected between the first and second oxidation waves of $1[\text{Ru}(\text{bpy})_2]_2^{4+}$ and the first and third oxidation waves of $1[\text{Ru}(\text{bpy})_2]_3^{6+}$. Such differences, however, are too small to be resolved in ordinary cyclic voltammograms. The reduction potentials are also very similar for the three mixed-ligand complexes. Since $1[\text{Ru}]^{2+}$ reduces at potentials less negative than those of $\text{Ru}(\text{bpy})_3^{2+}$ (Table II), the first reduction wave of the mixed-ligand complexes can be attributed to the reduction of the bpy-type coordinated arm(s) of the tripod ligand. The second and third reduction waves concern, of course, the bpy ligands of the $\text{Ru}(\text{bpy})_2^{2+}$ unit(s). The expected linear correlations^{2,39} between

spectroscopic and electrochemical quantities are verified.

Conclusions

No spectroscopic, photophysical, or electrochemical evidence has been found of an interaction between the metal-containing units in the binuclear and trinuclear complex. However, for the mononuclear complex $1[\text{Ru}(\text{bpy})_2]^{2+}$ there is clear evidence of electronic energy transfer with high efficiency from the noncoordinated arms of **1** to the metal-containing units. Presumably, such an interaction requires a perturbation energy so small (e.g., of the order of 10–100 cm^{-1}) that it cannot be detected in the spectroscopic and electrochemical measurements. It should also be noted, however, that the geometrical conformation of the bridging ligand **1** can be quite different in $1[\text{Ru}(\text{bpy})_2]^{2+}$ and $1[\text{Ru}(\text{bpy})_2]_3^{6+}$. In the monomer, the noncoordinated arms of **1** are likely to approach the ligands coordinated to the Ru center, giving a molecular structure quite different from that drawn in this paper to represent $1[\text{Ru}(\text{bpy})_2]^{2+}$. In the trimer, all the three arms of the tripod ligand **1** are coordinated to a Ru^{2+} center and thus will tend to stay away from each other, as shown by our schematic representation of this complex.

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Solvatochromism of Dinuclear Complexes: An Alternative Explanation

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The very large solvatochromism of the metal to ligand charge-transfer transitions in various, formally nonpolar, ligand-bridged dinuclear metal carbonyl complexes is discussed. The similarity of this behavior to that of related mononuclear species and the good correlations obtained with the "polar" part of McRae's equation are used to demonstrate that dipole-dipole interactions are the main cause of the solvatochromism. This contradicts previous explanations that have attributed the solvatochromism to changes in dispersion forces. It is concluded that, in the simplest approximation, the molecules may be regarded as having polar halves, each of which interacts with the solvent. Detailed interpretation in terms of McRae's equation is not possible without knowing whether the metal to ligand charge-transfer excited state is localized on one metal center or delocalized over both. The data available do not allow us to distinguish between these possibilities.

Introduction

Solvatochromism refers to changes in electronic absorption spectra with solvent. Although most, if not all, complexes are solvatochromic to some extent, the term is usually applied to species that show shifts in energy of at least a few hundred wavenumbers with variation in solvent. Many of the reports of solvatochromism in the inorganic literature involve $\text{M}(\text{CO})_4$ - (diimine) complexes, where M is Cr, Mo, or W.^{1–20} The solva-

chromic transition involves metal to ligand charge transfer (MLCT) from the d^6 Cr, Mo, or W core to the lowest energy π^* orbital of the diimine. These intense absorptions, which normally occur in the visible region, are, in most cases, blue shifted in polar

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