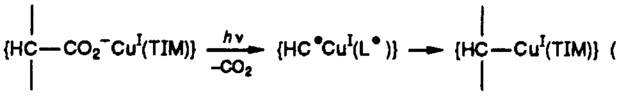
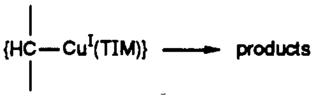


$$\{HC{-}CO_2^{-}Cu^{I}(TIM)\} \xrightarrow[-CO_2]{h\nu} \{HC^{\bullet}Cu^{I}(L^{\bullet})\} \rightarrow \{HC{-}Cu^{I}(TIM)\} \quad (19)$$



$$\{HC{-}Cu^{I}(TIM)\} \longrightarrow \text{products} \quad (20)$$

between a poly(acrylate)'s carboxylate and $Cu^{I}(TIM)^+$ is regarded.[9-12] It is improbable, however, that an ion-pair charge-transfer transition can be placed at energies as low as those in a charge transfer involving the electronic density of the TIM ligand. In terms of Jørgensen's optical electronegativities (eq 21),

$$\Delta\epsilon_{CT} = 35.8(\chi_L - \chi_M) + \Delta + \delta SPE + ... \quad (21)$$

reported values for the ligands, TIM and $-CO_2^-$, and Cu(I) suggest that the $-CO_2^-$ to Cu(I) transition is at a similar or lower energy than the energy of the Cu(I) to TIM transition.[9,13,14]

Experimental Section

Photochemical Procedures. Flash irradiations were carried out in experimental setups described elsewhere.[1,15] For flash-photolysis experiments with nanosecond time resolution, a Quanta Ray Nd Yag pumped dye laser was used as a source of 266-nm flashes with ca. 10-ns duration and 20-mJ energy. A mode-locked Yag laser was used as a source of 266-nm light pulses with ca. 18-ps width for measurements of spectra and reaction kinetics in a picosecond time domain. The apparatus used for the photogeneration and photolysis of transients has been described elsewhere and is based on the synchronous triggering of two lasers; it consists of a Questek excimer laser and a Candela flash-pumped dye laser for the respective photogeneration and photolysis of the Cu(I) complex.[6] In these flash-photolysis experiments, solutions of the complexes were deaerated with streams of ultrapure N_2.

Pulse Radiolysis. The apparatus and procedures used for the generation of the reduced macrocyclic complexes have been described elsewhere.[16] In these experiments, the solutions, ca. 10^{-4} M in a given complex, 6.0×10^{-4} M in poly(acrylate), and 0.1 M in 1,1-dimethylethanol, were deaerated with streams of ultrapure N_2. The alcohol scavenged the OH radicals, and carbon-centered secondary radicals exhibited no reactivity toward the macrocycle–poly(acrylate) complexes.

Materials. Aldrich poly(acrylic) acids with given formula weights were purified by dialysis according to a literature procedure.[1] The concentration of the poly(acrylic acids) was determined by titration with NaOH to neutral pH. Solutions of Cu^{II}(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^{2+}$–poly(acrylate) were prepared by adding appropriate amounts of the copper complex to solutions containing a known concentration of poly(acrylate) and adjusting the pH of the final solution to a value 6.5 with minute volumes of diluted NaOH or $HClO_4$ solutions as required. The compound [Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)]$(ClO_4)_2$ was prepared by a literature procedure and its purity established from its UV–vis absorption spectrum.[7,17] Other materials were reagent grade and used without further purification.

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Luminescent and Redox-Reactive Building Blocks for the Design of Photochemical Molecular Devices: Mono-, Di-, Tri-, and Tetranuclear Ruthenium(II) Polypyridine Complexes

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The syntheses, characterization, absorption spectra, luminescence spectra, luminescence lifetimes, and electrochemical behavior of 16 mono-, di-, tri-, and tetrametallic ruthenium(II) polypyridine complexes have been investigated. The general formulas of the complexes studied are $RuL_2(BL)^{2+}$, $L_2Ru(\mu\text{-}BL)RuL_2^{4+}$, $LRu[(\mu\text{-}BL)RuL_2]_2^{6+}$, and $Ru[(\mu\text{-}BL)RuL_2]_3^{8+}$, where L = 2,2′-bipyridine (bpy) or 2,2′-biquinoline (biq) and BL = 2,3- or 2,5-bis(2-pyridyl)pyrazine (dpp). The absorption spectra of the complexes exhibit broad and intense (ϵ up to ~50 000 M^{-1} cm^{-1}) metal-to-ligand charge-transfer (MLCT) bands, which in the oligonuclear complexes extend all over the visible region. All the complexes exhibit luminescence in the 600–850-nm region in a rigid matrix at 77 K (lifetimes of the order of 1 μs) and in fluid solution at room temperature (lifetimes of the order of 100 ns). Emissions can be assigned to specific metal–ligand chromophoric units, and the trends in the emission energies on changing ligands and/or nuclearity can be rationalized in the light of the trends observed for the potentials of first oxidation and first reduction processes. Corrected excitation spectra show that the luminescent excited state is populated with the same efficiency regardless of the excitation wavelength throughout the MLCT bands. In electrochemical experiments, the complexes show metal-centered oxidation and ligand-centered reduction processes. Most of the redox waves are reversible and can be assigned to specific metal(s) or ligand(s). The interaction between equivalent redox centers of the same complex is more or less weak, depending on the nature of BL and L. Each one of the mono-, di-, tri-, and tetranuclear complexes studied can be used as a building block for the design of luminescent and redox-reactive species containing a higher number of metal centers. Because of their broad and strong absorption bands in the visible region, relatively long luminescence lifetimes, and rich redox behaviors, complexes of this type can prove useful as antenna components for photosensitization purposes (including electron or hole injection on semiconductors), luminescence probes, and multielectron photocatalysts.

Introduction

A major research area in photochemistry is currently that concerning supramolecular systems capable of performing photoinduced energy migration and/or charge separation.[2-13] Such systems can be designed from building blocks that contain the

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Table I. Absorption and Luminescence Data

complex		absorption, 298 K[a]	luminescence				
			298 K[a]			77 K[c]	
no.	formula	λ_{max}, nm[b] (ϵ, 10^3 M^{-1} cm^{-1})	λ_{max}, nm	τ, ns[d]	$10^2\Phi$[e]	λ_{max}, nm	τ, μs
1	$Ru(bpy)_2(2,3\text{-dpp})^{2+}$[f]	475 sh (11.5)	691	240 (380)	2.3	628	4.18
2	$Ru(bpy)_2(2,5\text{-dpp})^{2+}$	486 (5.2)	695	270 (620)	4.1	647	2.40
3	$Ru(biq)_2(2,3\text{-dpp})^{2+}$	528 (7.6)	738	20		715	2.02
4	$Ru(biq)_2(2,5\text{-dpp})^{2+}$	527 (5.6)	737	15		715	2.15
5	$(bpy)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2^{4+}$[g]	527 (24.2)	802	102 (125)	0.3	709	2.00
6	$(biq)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(biq)_2^{4+}$	537 (15.6)	789	65		720	1.73
7	$(bpy)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(biq)_2^{4+}$	543 (22.4)	799	75		723	1.55
8	$(bpy)_2Ru(\mu\text{-}2,5\text{-dpp})Ru(bpy)_2^{4+}$	585 (15.9)	824	155		771	0.94
9	$(biq)_2Ru(\mu\text{-}2,5\text{-dpp})Ru(biq)_2^{4+}$	609 (11.5)	820	170		722	1.82
10	$(bpy)_2Ru(\mu\text{-}2,5\text{-dpp})Ru(biq)_2^{4+}$	595 (13.7)	830	190		792	1.00
11	$(bpy)Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2^{6+}$	545 (23.5)	804	75 (80)	0.1	721	1.78
12	$(bpy)Ru[(\mu\text{-}2,5\text{-dpp})Ru(bpy)_2]_2^{6+}$	595 (28.1)	831	65		767	0.98
13	$(bpy)Ru](\mu\text{-}2,3\text{-dpp})Ru(biq)_2]_2^{6+}$	546 (28.7)	773	140		713	2.18
14	$(bpy)Ru[(\mu\text{-}2,5\text{-dpp})Ru(biq)_2]_2^{6+}$	591 (22.9)	805	120 (190)	0.6	739	1.28
15	$Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_3^{8+}$[h]	545 (46.0)	811	50 (60)	0.1	727	1.38
16	$Ru[(\mu\text{-}2,3\text{-dpp})Ru(biq)_2]_3^{8+}$	610 (41.5)	795	130 (190)	0.1[i]	725	1.86

[a] Acetonitrile solution. [b] Lowest energy maximum. [c] MeOH/EtOH (4:1) rigid matrix. [d] Aerated solution; deaerated values in parentheses; experimental error ≤10%. [e] Deaerated solution; excitation in the lowest energy maximum; experimental error ≤20%. [f] Data in substantial agreement with those reported in ref 27, except for the luminescence quantum yield (0.92×10^{-2}); for other data, see refs 16 and 32. [g] Data in substantial agreement with those reported in ref 27, except for the luminescence quantum yield (0.025×10^{-2}); for other data, see refs 16 and 32. [h] See also refs 22 and 24. [i] Excitation wavelength 475 nm.

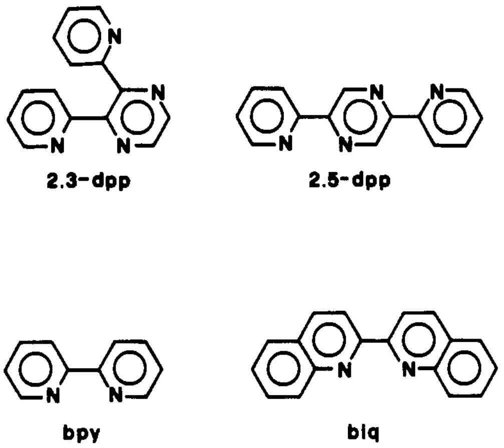

Figure 1. Structural formulas of the ligands.

necessary pieces of information (i.e., suitable absorption properties, excited-state energies, redox potentials, etc.) and bridging units that can link the building blocks in a suitable supramolecular structure. A number of systems of this type based on transition-metal complexes have been recently reported.[14-31]

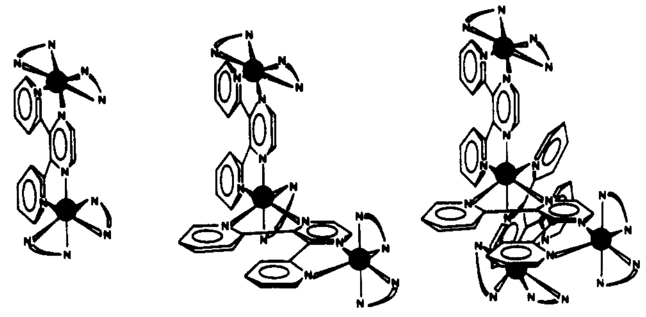

Figure 2. Schematic views of the structural formulas of the complexes (from left to right) $(N\text{-}N)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(N\text{-}N)_2^{4+}$, $(N\text{-}N)Ru[(\mu\text{-}2,3\text{-dpp})Ru(N\text{-}N)_2]_2^{6+}$, and $Ru[(\mu\text{-}2,3\text{-dpp})Ru(N\text{-}N)_2]_3^{8+}$. The chelating ligand schematized by N-N may be bpy or biq.

The 2,3- and 2,5-isomers of bis(2-pyridyl)pyrazine (dpp, Figure 1) are quite interesting bridging units, since they can coordinate luminescent and redox-reactive ML_2 building blocks (M = Ru(II), Os(II); L = bipyridine-type ligands).[16,22,24,27,32,33] Furthermore, coordination of dpp to Ru^{2+} and Os^{2+} gives rise to additional chromophoric and redox centers and the homo- and hetero-oligometallic complexes so obtained can be used as building blocks to design larger supramolecular species. Our laboratories are currently engaged in a systematic study along this direction.[24,34-36]

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Among the great variety of polypyridine ligands that can be used to obtain ML$_2$ units,[37] 2,2′-bipyridine (bpy) and 2,2′-biquinoline (biq) (Figure 1) are quite valuable, since their Ru(II) complexes are both luminescent and redox reactive. Furthermore, the Ru(bpy)$_2^{2+}$ and Ru(biq)$_2^{2+}$ units exhibit sufficiently different excited-state energies and redox potentials to allow specific assignment of their spectral bands and redox waves in the supramolecular species.

In this paper, we report the results of an investigation on 16 mono-, di-, tri-, and tetranuclear ruthenium(II) complexes obtained by using the bridging ligands (BL) 2,3-dpp and 2,5-dpp and the chelating ligands (L) bpy and biq (Figure 1). The structural formulas of the di-, tri-, and tetranuclear Ru(II) complexes of 2,3-dpp are schematized in Figure 2. The list of the complexes studied is given in Table I. Some of the complexes examined had been previously investigated in other[16,22,27,32,33] or our[24,35] laboratories.

Experimental Section

General Information. 2,3-Bis(2-pyridyl)pyrazine,[38] 2,5-bis(2-pyridyl)pyrazine,[39] Ru(bpy)$_2$Cl$_2$·2H$_2$O,[40] Ru(biq)$_2$Cl$_2$·2H$_2$O,[41] [Ru(bpy)Cl$_3$]$_n$,[42] and [Ru(2,3-dpp)$_3$](PF$_6$)$_2$[32] were prepared according to literature methods. All reactions were carried out under argon. All reactions, manipulations, and measurements involving biq derivatives were performed *in light-protected vessels. When not differently stated,* "ethanol" means the 95:5 (v/v) ethanol/water solution.

Details on equipment and procedures for conductivity, NMR spectra, absorption and emission spectra, and luminescence lifetimes and quantum yields have been previously reported.[34,43]

Electrochemical measurements were carried out at room temperature with a PAR 273 multipurpose equipment interfaced to a PC. The working electrode was either a Pt microelectrode or a hanging-mercury-drop electrode. The counter electrode was a Pt wire, and the reference electrode was a SCE separated with a fine glass frit. Tetraethylammonium perchlorate (polarographic grade) was used as supporting electrolyte. Cyclic voltammograms were usually obtained at a scan rate of 100 mV s^{-1}. Differential-pulse polarography was performed with a scan rate of 20 mV s^{-1}, a pulse height of 50 mV, and a duration of 50 ms. For reversible processes, half-wave potentials (vs SCE) were calculated as an average of the cathodic and anodic peaks. The criteria for reversibility were the separation between cathodic and anodic peaks (60 mV for monoelectronic processes), the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. The multielectron nature of some waves was inferred from comparison with the wave of Os(bpy)$_3^{2+}$ oxidation as an internal standard and from the comparison of different waves of the complex under investigation.

Experimental errors in the reported data are as follows: absorption maxima, 2 nm; emission maxima, 4 nm; emission lifetimes, 10%; luminescence quantum yields, 20%; redox potentials, 20 mV. As far as the extinction coefficients are concerned, the uncertainty in their absolute values is ~10% because of the highly diluted solutions used (10^{-5}–10^{-4} M).

Syntheses. [Ru(bpy)$_2$(2,3-dpp)](PF$_6$)$_2$ (1). A stirred suspension of Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.355 g, 0.68 mmol) in ethanol (20 mL) was slowly added to a refluxing solution of 2,3-dpp (0.240 g, 1.02 mmol) in ethanol (6 mL). The mixture was refluxed for 8 h and then rotary-evaporated in vacuo. The resulting material was dissolved in the smallest amount of 5:3 (v/v) water/acetone, and the solution was chromatographed on Sephadex-CM C-25 ion-exchange resin (column: 15 × 3 cm). Elution with 0.05 M NaCl in the above solvent system gave a pale brown fraction, which was discarded. The chloride form of complex **1** was eluted, raising the concentration of NaCl to 0.1 M (some remaining bordeaux red bimetallic species could be eluted with 0.3 M NaCl). The solution was partially evaporated in vacuo, and solid NH$_4$PF$_6$ was added until the precipitation was complete. The product was recovered as a brick red solid, dissolved in acetonitrile, precipitated with anhydrous ethanol, washed several times with anhydrous ethanol and then once with diethyl ether, and eventually dried in vacuo (72%).

[Ru(bpy)$_2$(2,5-dpp)](PF$_6$)$_2$ (2). The preparation was similar to the previous one. Employed quantities: Ru(bpy)$_2$Cl$_2$·2H$_2$O, 0.192 g (0.37 mmol) in ethanol (12 mL); 2,5-dpp, 0.130 g (0.55 mmol) in methanol (5 mL). Reflux duration: 6 h. Chromatographic and subsequent treatment procedures were similar to those for **1** (some dark green bimetallic species observed). Complex **2** was recovered as a brown solid (78%).

[Ru(biq)$_2$(2,3-dpp)](PF$_6$)$_2$ (3) and [Ru(biq)$_2$(2,5-dpp)](PF$_6$)$_2$ (4). To a light-protected solution of Ru(biq)$_2$Cl$_2$·2H$_2$O (0.050 g, 0.069 mmol; 1:1 (v/v) water/ethanol (9 mL)), previously refluxed for 12 h, was added a hot solution of the appropriate ligand (0.024 g, 0.101 mmol) in ethanol (3 mL), and the reflux was continued for 9 h (2,3-dpp) or 24 h (2,5-dpp). To the cooled reaction mixture was added an excess of solid NH$_4$PF$_6$. The product was recovered by filtration and washed several times with cold ethanol and then with diethyl ether. After drying, it was dissolved in dichloromethane and precipitated with ethanol, yielding a purple-red solid (76% and 61%, respectively).

{[Ru(bpy)$_2$]$_2$(μ-2,3-dpp)}(PF$_6$)$_4$ (5). A mixture of complex **1** (0.030 g, 0.032 mmol) and Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.0165 g, 0.032 mmol) in ethanol (10 mL) was refluxed for 12 h. After the mixture was cooled at room temperature and an excess of solid NH$_4$PF$_6$ was added, the product was recovered as a bordeaux red solid, which was washed several times with ethanol, dissolved in acetonitrile, precipitated with ethanol, washed with diethyl ether, and dried in vacuo (70%). Further purification, if necessary, could be obtained by the chromatographic procedure described for **1**.

{[Ru(biq)$_2$]$_2$(μ-2,3-dpp)}(PF$_6$)$_4$ (6). A mixture of complex **3** (0.060 g, 0.053 mmol) and Ru(biq)$_2$Cl$_2$·2H$_2$O (0.038 g, 0.053 mmol) in ethylene glycol (1.5 mL) was refluxed for 24 h and then cooled at room temperature and treated with a saturated aqueous solution of NH$_4$PF$_6$ (1.5 mL). The purple solid precipitate was washed several times with small amounts of cold ethanol. It was purified by several recrystallizations from dichloromethane/ethanol (60%).

[(bpy)$_2$Ru(μ-2,3-dpp)Ru(biq)$_2$](PF$_6$)$_4$ (7). Complex **1** (0.040 g, 0.043 mmol) and Ru(biq)$_2$Cl$_2$·2G$_2$O (0.031 g, 0.043 mmol) in ethylene glycol (1 mL) were reacted, and the product was treated as above. The recrystallization system was acetonitrile/ethanol. The final product was a purple red solid (87%).

{[Ru(bpy)$_2$]$_2$(μ-2,5-dpp)}(PF$_6$)$_4$ (8). In agreement with the method of Kaim et al.,[33] Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.050 g, 0.096 mmol) and 2,5-dpp (0.011 g, 0.048 mmol) were reacted in refluxing 10:1 (v/v) water/ethanol for 20 min. To the cooled reaction mixture was added an excess of solid NH$_4$PF$_6$. The dark green complex that precipitated was purified as described for **5** (80%).

{[Ru(biq)$_2$]$_2$(μ-2,5-dpp)}(PF$_6$)$_4$ (9). The reaction procedure was identical with that described for **6**. A purple solid recrystallized from dichloromethane/ethanol (65%).

[(bpy)$_2$Ru(μ-2,5-dpp)Ru(biq)$_2$](PF$_6$)$_4$ (10). The procedure was identical with that described for **7**. The final product was a dark green solid (76%).

[Ru(bpy)(2,3-dpp)$_2$](PF$_6$)$_2$ (A) and [Ru(bpy)(2,5-dpp)$_2$](PF$_6$)$_2$ (B). A stirred suspension of [Ru(bpy)Cl$_3$]$_n$ (0.114 g, 0.31 mmol) in 1:1 (v/v) water/ethanol (15 mL) was added to a refluxing solution of the appropriate ligand (0.147 g, 0.63 mmol) and trifluoroacetic acid (0.072 g, 0.63 mmol) in the same solvent system (6 mL). The reaction mixture was refluxed for 48 h, cooled to room temperature, neutralized by addition of 1 equiv of solid NaHCO$_3$, and dried in vacuo. The residue was dissolved in the smallest amount of 5:3 (v/v) water/acetone and chromatographed on Sephadex-CM C-25 ion-exchange resin (column: 15 × 3 cm). Elution with 0.05 M NaCl in the above system gave a fraction that was discarded. The chloride form of the complex was eluted, raising the concentration of NaCl to 0.1 M. The solution was evaporated in vacuo and the residue partially dissolved in anhydrous ethanol in order to remove most NaCl by filtration. A saturated aqueous solution of NH$_4$PF$_6$ was added until the precipitation was complete. The products were recovered as orange-brown solids that were recrystallized several times from dichloromethane/ethanol. Yields: A, 68%; B, 75%.

{Ru(bpy)[(μ-2,3-dpp)Ru(bpy)$_2$]$_2$}(PF$_6$)$_6$ (11) and {Ru(bpy)[(μ-2,5-dpp)Ru(bpy)$_2$]$_2$}(PF$_6$)$_6$ (12). A mixture of the appropriate precursor (A or B) (0.050 g, 0.049 mmol) and Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.052 g, 0.098 *mmol) in ethanol (15 mL) was refluxed for 48 h.* To the cold solution was added an excess of solid NH$_4$PF$_6$. The resulting solid (**11**, reddish brown; **12**, greenish blue) was washed several times with small amounts

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of ethanol and recrystallized from acetonitrile/ethanol. Yields: 80% and 65%, respectively.

{Ru(bpy)[(μ-2,3-dpp)Ru(biq)$_2$]$_2$}(PF$_6$)$_6$ (13) and {Ru(bpy)[(μ-2,5-dpp)Ru(biq)$_2$]$_2$}(PF$_6$)$_6$ (14). The amounts of the reagents and the procedures were similar to those of the previous preparation. Reaction solvent: ethylene glycol (2 mL). Refluxing time: 24 h. Precipitation medium saturated aqueous NH_4PF_6 solution (1 mL). Yields after recrystallization from acetonitrile/ethanol: **13** (bordeaux red solid), 68%; **14** (greenish blue solid), 70%.

{Ru[(μ-2,3-dpp)Ru(bpy)$_2$]$_3$}(PF$_6$)$_8$ (15). The procedure was different from that of Petersen et al.[22] A mixture of [Ru(2,3-dpp)$_3$](PF$_6$)$_2$ (0.036 g, 0.032 mmol) and Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.057 g, 0.097 mmol) in anhydrous ethanol (15 mL) was refluxed for 48 h. To the cooled solution was added an excess of solid NH_4PF_6, and the resulting purple solid was recrystallized several times from acetonitrile/ethanol, washed with ethanol and diethyl ether, and dried in vacuo (70%).

{Ru[(μ-2,3-dpp)Ru(biq)$_2$]$_3$}(PF$_6$)$_8$ (16). A mixture of [Ru(2,3-dpp)$_3$](PF$_6$)$_2$ (0.015 g, 0.014 mmol) and Ru(biq)$_2$Cl$_2$·2H$_2$O (0.029 g, 0.042 mmol) in ethylene glycol (3 mL) was refluxed for 18 h. After cooling, a saturated aqueous solution of NH_4PF_6 (2 mL) was added. The resulting purple-blue precipitate was washed several times with small amounts of cold ethanol and recrystallized several times from acetonitrile/ethanol, washed with diethyl ether, and dried in vacuo (82%).

Results

Syntheses and Characterization. Mononuclear species **1–4**, containing one dpp ligand, were prepared according to Scheme I. In comparison with its bpy analogue, the precursor complex Ru(biq)$_2$Cl$_2$ was less reactive toward both 2,3-dpp and 2,5-dpp. Furthermore, in contrast with previous observations, the latter ligand exhibited a reactivity lower than its isomer. In the preparations of mononuclear complexes **3** and **4**, the best yields and purities were obtained by adding the BL ligands only after a rather long reflux time, in order to allow the metal precursor to undergo to a great extent the aquation reaction in the absence of the bridging ligand. For oligonuclear compounds it was necessary to raise the reaction temperature to that of refluxing ethylene glycol. Due to the light sensitivity of all derivatives containing biq, their purification was accomplished by recrystallization.

Scheme I

$$\mathrm{RuL_2Cl_2} + 2,n\text{-dpp} \xrightarrow{\mathrm{NH_4PF_6}} [\mathrm{RuL_2}(2,n\text{-dpp})](\mathrm{PF_6})_2$$

The most convenient general route to dinuclear homoligated complexes **5**, **6**, and **9** (Scheme II) consisted of two separate steps. This was obviously compulsory for the preparation of the heteroligated complexes **7** and **10** (Scheme III); the choice of **1** and **2**, instead of **3** and **4**, as precursors was dependent on their easier preparation and purification, while the more drastic reaction conditions did not cause undesired consequences. In order to prepare the trinuclear complexes **11–14** (Scheme IV), we had to realize the synthesis of their precursors A and B. These were obtained in satisfactory yields by reacting [Ru(bpy)Cl$_3$]$_n$ with the appropriate bridging ligand in the presence of trifluoroacetic acid (1:2:2). This procedure prevented the massive formation of polymeric species by deactivating a chelating site of BL through protonation. The subsequent reactions were then carried out by using purified intermediates.

Scheme II

$$\mathrm{RuL_2Cl_2} + [\mathrm{RuL_2}(2,n\text{-dpp})]^{2+} \xrightarrow{1:2} \xrightarrow{\mathrm{NH_4PF_6}} [(\mathrm{RuL_2})_2(\mu\text{-}2,n\text{-dpp})](\mathrm{PF_6})_4$$

Scheme III

$$\mathrm{Ru(biq)_2Cl_2} + [\mathrm{Ru(bpy)_2}(2,n\text{-dpp})]^{2+} \xrightarrow{1:2} \xrightarrow{\mathrm{NH_4PF_6}} [(\mathrm{bpy})_2\mathrm{Ru}(\mu\text{-}2,n\text{-dpp})\mathrm{Ru(biq)_2}](\mathrm{PF_6})_4$$

Scheme IV

$$[\mathrm{Ru(bpy)Cl_3}]_n + 2,n\text{-dpp} \xrightarrow{1:2} \xrightarrow{\mathrm{NH_4PF_6}} [\mathrm{Ru(bpy)}(2,n\text{-dpp})_2](\mathrm{PF_6})_2$$

$$[\mathrm{Ru(bpy)}(2,n\text{-dpp})_2](\mathrm{PF_6})_2 + \mathrm{RuL_2Cl_2} \xrightarrow{1:2} \xrightarrow{\mathrm{NH_4PF_6}} \{\mathrm{Ru(bpy)}[(\mu\text{-}2,n\text{-dpp})\mathrm{RuL_2}]_2\}(\mathrm{PF_6})_6$$

The synthesis of tetranuclear complexes (Scheme V) by reacting [Ru(dpp)$_3$]$^{2+}$ with the appropriate counterpart has been limited to the derivatives of 2,3-dpp. Up to now, attempts to prepare the analogous 2,5-dpp precursor were unsuccessful, due to the great tendency of this ligand to behave as a bischelating agent toward Ru(bpy)$_2$Cl$_2$, irrespective of the reaction conditions and molar ratios employed.

Scheme V

$$[\mathrm{Ru}(2,3\text{-dpp})_3]^{2+} + \mathrm{RuL_2Cl_2} \xrightarrow{1:3} \xrightarrow{\mathrm{NH_4PF_6}} \{\mathrm{Ru}[(\mu\text{-}2,3\text{-dpp})\mathrm{RuL_2}]_3\}(\mathrm{PF_6})_8$$

For all of the novel complexes, satisfactory elemental analyses and consistent IR spectra and conductivity values (supplementary data) were obtained. Infrared spectra were of great diagnostic value in order to detect, or rule out, the presence of dpp and μ-dpp. In fact, in mononuclear complexes a weak band with a maximum at 990 cm^{-1} was always present, which disappeared in bridged derivatives. Furthermore, μ-2,3-dpp complexes showed two characteristic bands of medium intensity at 610 and 580 cm^{-1}.

The structural characterization of the complexes is an open problem because it was impossible to grow crystals suitable for diffractometric analysis, and the ^{1}H NMR spectra were complicated by the high number of hydrogens reasonant in a narrow spectral region, even in mononuclear species. Furthermore, taking into account that each metal is a chiral center, the products of nuclearity greater than 1 are mixtures of diastereoisomeric species.[33] Evidence concerning the structure around the central metal would be necessary in particular for tri- and tetranuclear compounds, where three or two geometrical arrangements of the chelating ligands, respectively, can exist. The problem might be dealt with (i) by simplifying NMR spectra by use of perdeuterio L ligands[44] and (ii) by preparing the complexes from enantiomerically resolved precursors and by separating the diastereoisomeric products. If the configurations (optical and geometrical) of precursors are stable enough under the reaction and purification conditions, it would be possible, through a combination of these two techniques, to obtain products suitable for NMR analysis. Of course the requirements for crystal structure determinations would also be fulfilled. We plan to devote some experimental effort to this problem in the near future.

Spectroscopic, Photophysical, and Electrochemical Measurements. All complexes examined were stable under the experimental conditions used. The absorption spectra in acetonitrile solution show very intense (ϵ_{max} 30 000–240 000 M^{-1} cm^{-1}) bands in the UV region and broad, intense (ϵ_{max} 7000–50 000 M^{-1} cm^{-1}) bands in the visible region, which account for the beautiful colors (from red to green to blue) exhibited by the complexes. Figure 3 shows the spectra of the mono-, di-, tri-, and tetrametallic complexes that contain the 2,3-dpp bridging ligand (BL) and bpy chelating ligand (L). Figure 4 shows the spectra of the analogous family with L = biq. Figures 5 and 6 show the spectra of the dinuclear complexes with BL = 2,3-dpp and 2,5-dpp, respectively. Table I summarizes the wavelengths and extinction coefficients of the maxima at lowest energy.

All the complexes examined are luminescent, both in a rigid matrix at 77 K and in fluid solution at room temperature. The luminescence bands at room temperature of some of the complexes studied are shown in the insets of Figures 3 and 4. For some complexes, namely **5**, **11**, **14**, and **15**, corrected excitation spectra in the visible region were also recorded and were found to match closely the corresponding absorption spectra. No luminescence rise time was observed, and the luminescence decay was monoexponential in all cases. The corrected maxima of the luminescence bands, the luminescence lifetimes, and the luminescence quantum yields are gathered in Table I.

The electrochemical experiments showed that the complexes undergo several redox processes in the potential window examined (+1.80/−2.00 V). Most of the observed waves are reversible. In

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Table II. Electrochemical Data[a]

complex		$E_{1/2}$, V							
no.	formula	oxidation		reduction					
	$Ru(bpy)_3^{2+}$ [b]		+1.26	−1.35	−1.54	−1.79			
	$Ru(bpy)_2biq^{2+}$ [b]		+1.33	−0.91	−1.37	−1.66			
1	$Ru(bpy)_2(2,3\text{-dpp})^{2+}$ [c]		+1.31	−1.06	−1.55	−1.74			
2	$Ru(bpy)_2(2,5\text{-dpp})^{2+}$		+1.33	−1.03	−1.52	−1.71	−1.89		
3	$Ru(biq)_2(2,3\text{-dpp})^{2+}$		+1.47	−0.79	−0.98	−1.40	−1.81		
4	$Ru(biq)_2(2,5\text{-dpp})^{2+}$		+1.45	−0.80	−1.02	−1.31	−1.81		
5	$(bpy)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2^{4+}$ [c]	+1.55	+1.38	−0.67	−1.17	−1.57[d]	−1.89[d]		
6	$(biq)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(biq)_2^{4+}$		(+1.57)[e]	−0.45	−0.81[d]	−0.95	−1.19[d]		
7	$(bpy)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(biq)_2^{4+}$	+1.48	+1.36	−0.68	−1.18	−1.57[d]	−1.81[d]		
8	$(bpy)_2Ru(\mu\text{-}2,5\text{-dpp})Ru(bpy)_2^{4+}$ [f]	+1.54	+1.37	−0.53	−1.08	−1.50[d]	−1.81[d]		
9	$(biq)_2Ru(\mu\text{-}2,5\text{-dpp})Ru(biq)_2^{4+}$		(+1.48)[e]	−0.45	−0.82[d]	−0.99	−1.26[d]		
10	$(bpy)_2Ru(\mu\text{-}2,5\text{-dpp})Ru(biq)_2^{4+}$		(+1.43)[e]	−0.47		overlapping waves			
11	$(bpy)Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2^{6+}$		+1.48[d]	−0.55	−0.75	−1.17	1.47[d]	1.75[d]	
12	$(bpy)Ru[(\mu\text{-}2,5\text{-dpp})Ru(bpy)_2]_2^{6+}$		+1.45[d]	−0.48	−0.60	−1.10	−1.30	−1.52	
13	$(bpy)Ru[(\mu\text{-}2,3\text{-dpp})Ru(biq)_2]_2^{6+}$		+1.60[d]	−0.47[d]	−0.87[d]	−1.17[d]	−1.50	−1.79[d]	
14	$(bpy)Ru[(\mu\text{-}2,5\text{-dpp})Ru(biq)_2]_2^{6+}$		+1.57[d]	−0.47[d]	−0.89[d]	−1.21[d]	−1.53	−1.78[d]	
15	$Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_3^{8+}$		+1.50[g]	−0.56	−0.63	−0.70	−1.20	−1.33	−1.48
16	$Ru[(\mu\text{-}2,3\text{-dpp})Ru(biq)_2]_3^{8+}$		+1.58[g]	(−0.6)[h]	−0.87[g]	−1.15[g]			

[a] Acetonitrile solution, room temperature; $E_{1/2}$ values vs SCE; monoelectronic waves unless otherwise noted. At more negative potentials, overlapping and/or irreversible waves are present; experimental error ±20 mV. [b] From ref 41. [c] See also refs 16, 27, and 32. [d] Dielectronic wave. [e] Large wave, presumably corresponding to a two-electron process. [f] See also ref 33. [g] Trielectronic wave. [h] Large wave, presumably corresponding to a three-electron process.

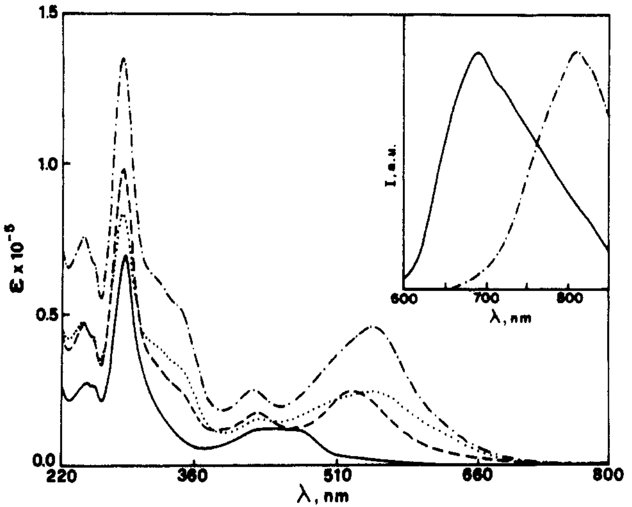

Figure 3. Absorption spectra of $Ru(2,3\text{-dpp})(bpy)_2^{2+}$ (—), $(bpy)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2^{4+}$ (- - -), $(bpy)Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_2^{6+}$ (···), and $Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_3^{8+}$ (–·–·). The inset shows the corrected luminescence spectra of the mono- and tetrametallic complexes.

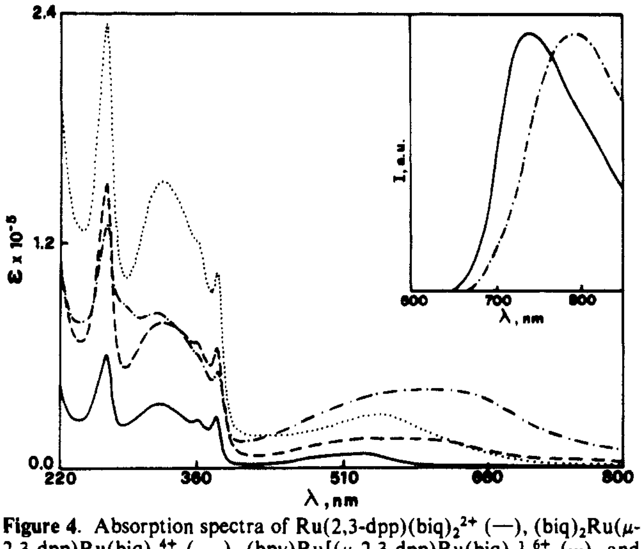

Figure 4. Absorption spectra of $Ru(2,3\text{-dpp})(biq)_2^{2+}$ (—), $(biq)_2Ru(\mu\text{-}2,3\text{-dpp})Ru(biq)_2^{4+}$ (- - -), $(bpy)Ru[(\mu\text{-}2,3\text{-dpp})Ru(biq)_2]_2^{6+}$ (···), and $Ru[(\mu\text{-}2,3\text{-dpp})Ru(biq)_2]_3^{8+}$ (–·–·). The inset shows the corrected luminescence spectra of the mono- and tetranuclear complexes.

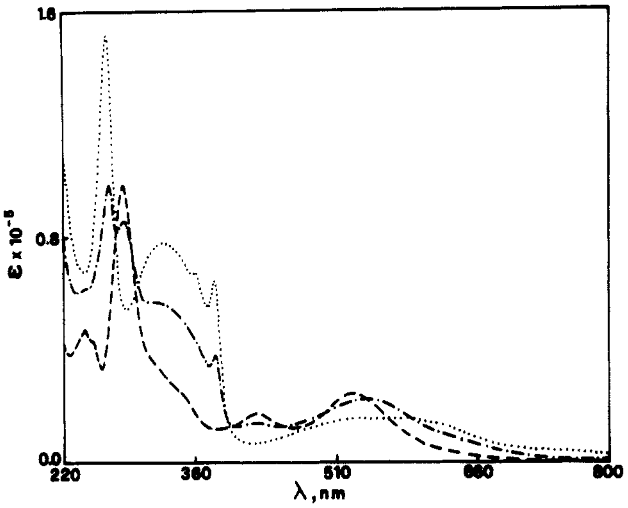

Figure 5. Absorption spectra of the $[L_2Ru(\mu\text{-}2,3\text{-dpp})L'_2]^{4+}$ complexes: L = L′ = bpy (- - -); L = L′ = biq (···); L = bpy, L′ = biq (–·–·).

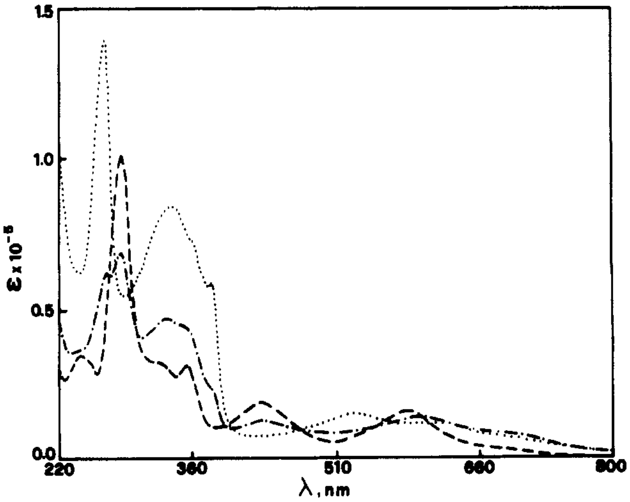

Figure 6. Absorption spectra of the $[L_2Ru(\mu\text{-}2,5\text{-dpp})RuL'_2]^{4+}$ complexes: L = L′ = bpy (- - -); L = L′ = biq (···); L = bpy, L′ = biq (–·–·).

the oligometallic complexes, wave overlapping is frequent, especially when L = biq. Some waves are di- or trielectronic in nature. The potential values are collected in Table II.

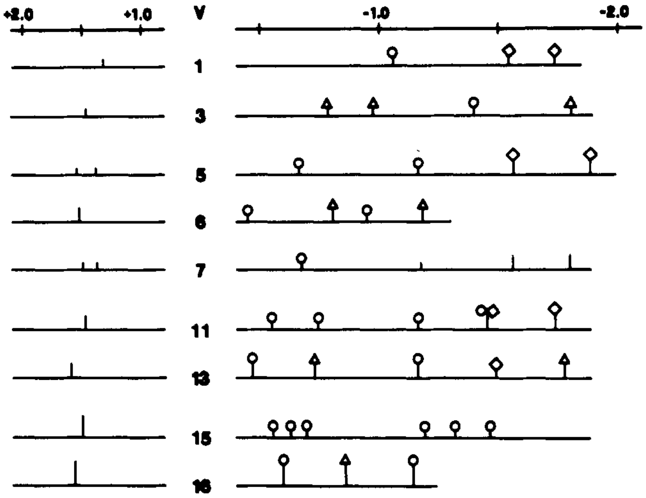

Figure 7. Schematic comparison of the redox potentials for the complexes of 2,3-dpp. The complexes are numbered as in the tables. The height of each vertical line is proportional to the number of electrons involved (1, 2, or 3). Assignment of the reduction waves to the various ligands is indicated by circles (dpp), triangles (biq), and diamonds (bpy).

Discussion

The spectroscopic and electrochemical properties of mononuclear transition-metal complexes are usually discussed with the assumption that the ground as well as the excited and redox states involved can be described in a sufficiently approximate way by localized molecular orbital configurations.[45-47] With such an assumption, the various spectroscopic transitions are classified as metal-centered (MC), ligand-centered (LC), or charge-transfer (either metal-to-ligand, MLCT, or ligand-to-metal, LMCT).[45] In the same way, the oxidation and reduction processes are classified as metal- or ligand-centered.[47] For complexes that contain different ligands, both excited states and redox forms of each specific ligand can often be distinguished. This simplified picture is generally applicable to mononuclear Ru(II) polypyridine complexes.[37] The localized molecular orbital approach, of course, can also be applied to polynuclear complexes constituted of weakly coupled units. Examples of bridging ligands that only allow a very weak interaction are 4,4′-bipyridine,[48] its phenylene-spaced derivatives[49] $bpy(CH_2)_n$–C_6H_4–$(CH_2)_n bpy$,[21] and the tris(bipyridyl) tripod $C_5H_3(CH_2NR$–CO–$bpy)_3$.[31] For such complexes, excitation and redox processes concerning specific ligands and specific metals can be distinguished. The 2,3- and 2,5-dpp bridges may allow a noticeable coupling between the bridged units, but we will see that a localized molecular orbital configuration approach can still be used as a first approximation to rationalize and correlate the electrochemical and spectroscopic results obtained for the oligometallic complexes examined in this paper.

Electrochemistry. For assignment and correlation purposes, we will make use of the data reported in Table II as well as the schemes of Figures 7 and 8, where we have shown schematically the potentials and the number of electrons involved in the reversible oxidation and reduction processes observed for the complexes of the 2,3-dpp and 2,5-dpp families.

The data available for the mononuclear complexes $Ru(bpy)_2L^{2+}$ (L = bpy, 2,3-dpp, 2,5-dpp, biq) and $Ru(biq)_2L^{2+}$ (L = 2,3-dpp, 2,5 dpp) show that the (metal-centered) oxidation potential increases in the series bpy < 2,3-dpp < 2,5-dpp ≤ biq. This, of course, shows that the amount of negative charge localized on the metal decreases in the same order along the ligand series. The (ligand-centered) reduction potentials of the same complexes show that the potential for coordinated ligand reduction decreases in the series biq > 2,5-dpp > 2,3-dpp > bpy. The oxidation waves and most of the reduction waves observed for the di-, tri-, and tetranuclear complexes can be assigned on the basis of the above ligand series.

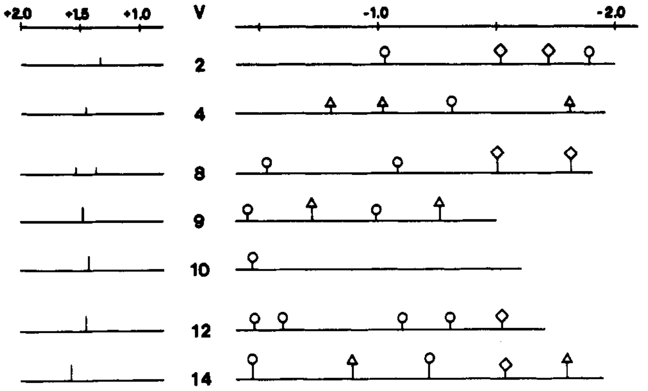

Figure 8. Schematic comparison of the redox potentials for the complexes of 2,5-dpp. For details, see caption of Figure 7.

The behavior of the dinuclear complexes (Table II, Figures 7 and 8) can be rationalized if they are seen as mononuclear $Ru(L)_2BL^{2+}$ species that carry the electron acceptor $Ru(L)_2^{2+}$ substituent on BL.[16,19] Because of the electron donation from μ-BL to the "substituent", some negative charge is also transferred from the "first" Ru to μ-BL, with a consequent shift of the oxidation potential to more positive values. The oxidation of the "second" Ru ion is further displaced to more positive potentials, which shows that the two metals are coupled via μ-BL. The latter effect is smaller for L = biq compared to L = bpy, as expected because biq leaves less electronic density on the metal, with a consequent lower ability of the metal to buffer the lack of electronic charge in another site of the molecule. In the bpy–biq mixed-ligand species, the first metal to be oxidized is obviously that of the bpy unit.

The reduction waves of the dinuclear complexes can be assigned to specific ligands. As mentioned above, the coordination of the electron acceptor $Ru(L)_2^{2+}$ moiety to BL decreases the electronic density on the bridging ligand. Therefore, BL becomes much easier to reduce in the dinuclear than in the mononuclear complexes. This is clearly shown by Figures 7 and 8. In **5** and **8** the first two reduction waves are monoelectronic and can be assigned to successive one-electron reduction of μ-BL. The splitting between these two waves is very high (~0.50 V), as expected for two electrons that enter on the same ligand, and it is slightly smaller for 2,3-dpp, in agreement with the distortion from a planar geometry (with consequent loss of conjugation) in the 2,3-dpp isomer. The other two reduction waves of **8** at more negative potentials are dielectronic and can be straightforwardly assigned to the successive reductions of couples of bpy coordinated to different metals.[16,32,33] The situation is different for **6** and **9** (Figures 7 and 8). The first and third reduction waves are monoelectronic, while the second and fourth waves are dielectronic. This behavior allows us to assign the first wave to one-electron reduction of μ-BL, the second wave to one-electron reduction of two biq ligands that reside on different metals, the third wave to the second one-electron reduction of μ-BL, and the fourth wave to the first one-electron reduction of the other two biq ligands. The behavior of the mixed-ligand complexes **7** and **10** is complicated. The first reduction wave is monoelectronic and concerns the BL moiety coordinated to the $Ru(biq)_2^{2+}$ component, which is a better electron-withdrawing substituent than $Ru(bpy)_2^{2+}$. As far as the successive waves are concerned, for the 2,3-dpp complex **7** it is not clear whether the second reduction wave involves the bridge or biq, and the assignment of the following waves is therefore uncertain. For the 2,5-dpp complex **10**, assignment is precluded by wave overlapping.

Each one of the four trinuclear complexes **11**–**14** shows a two-electron oxidation wave that can be assigned to the one-electron oxidation of the terminal Ru ions. Again, the bpy-co-

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ordinated ruthenium is easier to oxidize than the biq-coordinated one. Evidence for a further oxidation wave, which would concern the central metal, appears at the limit of the potential window examined.

The reduction pattern of the trimetallic complexes can be better understood by viewing the complex as containing two equivalent L_2RuBL groups "bridged" by a $(bpy)Ru^{2+}$ unit. The clearest pattern is shown by **12**. The first two one-electron reduction waves correspond to reduction of the two equivalent (and slightly interacting) μ-BL groups, presumably on their moieties that are coordinated to the $Ru(bpy)^{2+}$ unit. The two following waves concern the second one-electron reduction of the same μ-BL ligands on the other coordinating moieties. The fifth wave must concern a bpy ligand; since it is a one-electron, well-isolated wave, we assign it to the bpy of the $(bpy)Ru^{2+}$ unit that bridges the two equivalent μ-BL groups (see also below). The behavior of the analogous complex **14** can be easily understood when one considers that biq is much easier to reduce than bpy and that $Ru(biq)_2^{2+}$ is a better electron-withdrawing group than $Ru(bpy)_2^{2+}$. For the latter reason, the two bridging ligands are more isolated and each couple of one-electron reduction waves of the two μ-BL merges into a two-electron wave. Between such dielectronic waves, another dielectronic wave appears, which can be assigned to one-electron reduction of two biq ligands, each one coordinated to one of the two equivalent, terminal ruthenium ions. The successive one-electron wave can be assigned to the reduction of the bpy ligand coordinated to the central ruthenium, and the following two-electron wave to the reduction of the last two biq ligands. It should be noted that as many as nine electrons can be reversibly added to this complex at potentials more positive than −1.8 V, one for each chelating ligand site. The behavior of the two trimetallic complexes of 2,3-dpp, **11** and **13**, is quite similar to that of the analogous 2,5-dpp complexes.

The two tetrametallic complexes **15** and **16** (Figure 7) show a trielectronic oxidation wave, which involves the three equivalent peripheral metals. The oxidation of the central metal cannot be observed. As far as reduction is concerned, for the bpy complex **15** there are three, close lying, one-electron waves that correspond to the reduction of the three μ-BL groups.[22] The second triplet of one-electron waves, which is present at more negative potentials, can be assigned to the second reduction of the bridging ligands. The wave that follows ($E_{pc} = -1.75$ V) is irreversible, and it should involve reduction of bpy ligands coordinated to the three peripheral metals. The behavior of the tetrametallic complex containing biq **16** is similar, except that each one of the two triplets gives rise to a trielectronic wave. This can be rationalized by taking into account the above mentioned difference in the electron-withdrawing properties of the $Ru(biq)_2^{2+}$ units compared with the $Ru(bpy)_2^{2+}$ ones. Between these waves, another trielectronic wave appears, which is due to one-electron reduction of three biq ligands coordinated to the peripheral metals.

In conclusion, the electrochemical behavior of the complexes examined can be satisfactorily rationalized. Oxidation is metal centered, and the observed trend in the oxidation potentials reflects the decreasing electron-donor capacity (taking into account both σ-donation and π-acceptance) of the coordinated units in the "ligand" series bpy > 2,3-dpp > 2,5-dpp > biq > $(\mu\text{-2,3-dpp})Ru(bpy)_2^{2+} \geqslant (\mu\text{-2,5-dpp})Ru(bpy)_2^{2+} > (\mu\text{-2,3-dpp})Ru(biq)_2^{2+} \geqslant (\mu\text{-2,5-dpp})Ru(biq)_2^{2+}$ for the mono- and dinuclear compounds. For higher oligomers, more complex "ligands" should be considered. Reduction is ligand centered, and the ligands that are easier to reduce are the bridged dpp ligands. In passing from the dimetallic to the trimetallic and tetrametallic complexes, the number of μ-BL groups increases from 1 to 2 and 3 so that the reduction pattern begins with a singlet, a doublet, and a triplet, respectively. The splitting of the multiplet components depends on the type of bridged and peripheral ligands.

Absorption Spectra. In the electronic absorption spectra of the complexes examined (Table I, Figures 3–6), one can distinguish two main regions. Below 400 nm there are very intense absorption bands that correspond to ligand-centered (LC) transitions. Comparison with the spectra of the homoleptic $Ru(bpy)_3^{2+}$, $Ru(biq)_3^{2+}$, and $Ru(2,3\text{-dpp})_3^{2+}$ and of the mixed-ligand $Ru(bpy)_2L^{2+}$ (L = biq, 2,3-dpp, 2,5-dpp) complexes allows us to assign the narrow bands at 380 and 360 nm and the very intense band at 262 nm to the biq ligands, the broad absorption in the 300–350-nm region to the dpp ligands, and the band at 282 nm to bpy. In this region dominated by the LC transitions, the absorption spectra are roughly additive.

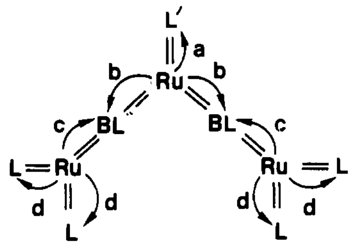

Figure 9. Schematic representation of the trinuclear complexes and of the expected types of "proximate" MLCT transitions.

For λ > 400 nm the spectra are dominated by moderately intense bands that can be assigned to MLCT transitions. From the spectra of the parent mononuclear homoleptic and heteroleptic complexes and from the above discussed electrochemical data, the energy order of the metal-to-ligand charge-transfer transitions is expected to be the following: Ru → bpy > Ru → 2,3-dpp > Ru → 2,5-dpp > Ru → biq > Ru → μ-2,3-dpp > Ru → μ-2,5-dpp. It should be noted, however, that in the oligometallic complexes the metals may be not equivalent because of a different coordination environment and that the two coordinating moieties of a bridging ligand are not equivalent when they bridge different metal units. For example, in the trimetallic complexes as many as four different types of MLCT transitions between proximate centers are expected (Figure 9). Under such conditions, a great number of overlapping waves are present and detailed assignments become difficult. Further complications may arise from interchromophoric coupling, as pointed out by De Armond and co-workers,[50] and from CT transitions between remote centers.[13] In spite of these difficulties, the general features of each spectrum and the band shifts on changing the type of ligand and/or the number of metals can be fairly well rationalized.

For a brief discussion of the main spectral features, we will make reference to the spectra reported in Figures 3–6. The spectrum of **1** (Figure 3) shows a broad absorption between 400 and 500 nm, which receives contributions from Ru → bpy and Ru → 2,3-dpp transitions, the latter being at lower energy.[16,24,27,32] In the dimetallic complex **5** (Figure 3), the bridging ligand becomes easier to reduce (see previous section) and, as a consequence, the Ru → 2,3-dpp band moves to lower energies. At the same time, the Ru → bpy band moves slightly to the blue because in the dinuclear complex the metal ions are slightly more difficult to oxidize than in the mononuclear complex. For the tri- and tetrametallic species, the most noticeable result is the increase in intensity of the Ru → μ-2,3-dpp band compared to the Ru → bpy band because of the increasing ratio between the number of Ru(2,3-dpp) and the Ru(bpy) chromophoric units.

In the spectra of the analogous biq compounds (Figure 4) there is an extended overlap between the Ru → μ-2,3-dpp and the Ru → biq bands. In the mononuclear complex, the Ru → biq band is expected to lie at longer wavelengths than the Ru → 2,3-dpp band, but in the oligonuclear complexes, the reverse is expected because of the low electron density on the bridging ligand. Figures 5 and 6 clearly show the displacement of the visible absorption toward the red when bpy is replaced by biq in the dimetallic complexes. Such a replacement causes the disappearance of the Ru → bpy band at ~420 nm and the appearance of the Ru → biq absorption at ~540 nm. As far as the Ru → dpp bands are concerned, they would be expected to move slightly to higher energy because biq decreases the electronic charge on Ru (see

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also the electrochemical results). However, the observed trend is a strong increase in intensity toward the red, perhaps because of interchromophoric coupling effects.[50]

Luminescence Spectra and Decays. All the complexes examined exhibit an emission band in the red region of the spectrum (Table I). As usually happens for Ru(II) polypyridine complexes, such an emission originates from the lowest triplet metal-to-ligand charge-transfer excited state. Comparison with the spectroscopic and electrochemical data of the parent homoleptic complexes[37] shows that the luminescence of $\mathrm{Ru(bpy)_2BL^{2+}}$ originates from a Ru → BL level. For the $\mathrm{Ru(biq)_2(BL)^{2+}}$ complexes, however, luminescence originates from a Ru → biq level, as shown by the fact that the two biq complexes emit at the same wavelength and at lower energy than the bpy ones (while the reverse would be expected for emission from a Ru → BL level).

For the dimetallic complexes, electrochemistry suggests that the lowest excited state is a Ru → μ-BL level in all cases. This is supported by the observation that, at room temperature, the bpy and biq complexes emit at approximately the same wavelengths (~800 nm for BL = 2,3-dpp and ~825 nm for BL = 2,5-dpp). At 77 K, however, the situation is complicated because the energies of the Ru → biq CT levels are only slightly dependent on temperature,[37] whereas the energies of the Ru → BL levels (especially for 2,3-dpp) are more sensitive to temperature not only in the mononuclear but also in the oligonuclear species (Table I). This may lead to a reverse energy ordering of the Ru → BL and Ru → biq levels on changing temperature, as appears to be the case for complexes **6** and **9**, whose emission energy at 77 K does not depend on the bridging ligand. For the bpy–biq mixed dinuclear complexes when BL = 2,5-dpp, the emission energy is lower than that of **8**, which suggests a Ru → 2,5-dpp emission even at 77 K. But for the dinuclear 2,3-dpp bpy–biq complex, emission occurs at practically the same wavelength as for **6**, which indicates that luminescence takes place from a Ru → biq CT level. In conclusion, for the dimetallic complexes at low temperature the energy of the lowest excited state decreases in the series (BL)Ru → bpy > $\mathrm{(biq)_2Ru}$ → 2,3-dpp > $\mathrm{(biq)_2Ru}$ → 2,5-dpp > $\mathrm{(bpy)_2Ru}$ → 2,3-dpp > (BL)Ru → biq > $\mathrm{(bpy)_2Ru}$ → 2,5-dpp. It should also be noted that the lowest Ru → μ-dpp and Ru → biq CT levels involve different Ru ions in the bpy–biq dinuclear complex.

In the trinuclear complexes luminescence can be assigned to Ru → μ-dpp CT levels, in agreement with the reduction potentials. The dielectronic nature of the first oxidation wave suggests that the lowest excited level involves external Ru ions. The blue shift from the bpy to the biq complexes is due to the lower electron donor capacity of biq compared to bpy.

In the tetranuclear bpy complex luminescence should originate from the peripheral Ru → μ-2,3-dpp CT levels because the bridged 2,3-dpp ligand is easier to reduce than bpy and the peripheral ruthenium ions carry a larger negative charge than the central one owing to the better donor properties of bpy compared with bridged 2,3-dpp.[22,24] In the biq complex, emission from a Ru → biq level can be ruled out because it would be expected to occur at $\lambda < 738$ nm from the behavior of the $\mathrm{Ru(biq)_2(2,3\text{-}dpp)^{2+}}$ complex.

It should be pointed out that corrected emission spectra in the visible region of **5**, **11**, **14**, and **15** have shown that the luminescence quantum yield is independent of excitation wavelength. This indicates that the luminescent level is populated with the same (presumably unitary) efficiency on excitation of the various CT bands. Thus, in the tri- and tetrametallic complexes there is energy transfer from the central to the peripheral chromophores. When the central Ru ion is replaced by Os, energy transfer occurs in the reverse direction and all of the energy is collected in the central chromophoric unit (antenna effect).[24]

It should be recalled[11,13,51] that in polymetallic complexes the deactivation of upper CT excited states to the lowest one can be viewed either as radiationless transitions between levels of a "large molecule" or as energy or electron transfers between various components of a "supramolecular" species. For example, for the complexes shown in Figure 9, deactivation of the Ru → L′ CT level that can be obtained with excitation *a* to the lower lying Ru → dpp CT level that can be obtained by excitation *b* can be described as (i) interconversion between excited states of the $\mathrm{L_2RuBLRu(L')BLRuL_2^{6+}}$ ion, (ii) energy transfer between the Ru(L′) and Ru(BL) chromophoric groups, or (iii) electron transfer from L′ to BL.

All of the complexes examined show luminescence lifetimes of the order of microseconds at 77 K, as expected for MLCT levels of Ru(II) polypyridine complexes. From the measured luminescence quantum yields and lifetimes at room temperature, one can evaluate radiative rate constants, k_r, in the range 10^4–10^5 $\mathrm{s^{-1}}$. On the assumption that k_r does not depend on T, it follows that τ(77 K) is largely determined by the rate of radiationless decay, k_{nr}. A plot of ln $(1/\tau)$ vs the energy of the luminescent level is (roughly) linear, as expected from the energy gap law.[51,52] At room temperature, the luminescence lifetime is much shorter in all cases, and the lifetime values do not obey the energy gap law, as happens when activated radiationless decays, possibly related to photodecomposition reactions, take place.[37]

When the orbital involved in the first reduction process is the same as that involved in the MLCT absorption and emission processes, for $\mathrm{RuL_3^{2+}}$ complexes a linear correlation is generally observed,[37,53–55] between the energy of the absorption or emission maxima and the quantity $\Delta E_{1/2} = [E_{1/2}(\mathrm{RuL_3^{3+/2+}}) - E_{1/2}(\mathrm{RuL_3^{2+/+}})]$. For our complexes the linear correlation between $\Delta E_{1/2}$ and the maximum of the luminescence band at room temperature is substantially obeyed. Because of the broadness and overlapping of the absorption bands, it is not possible to correlate $\Delta E_{1/2}$ with the absorption maximum.

Metal–Metal Interaction. In the recent literature on oligometallic complexes, there are often discussions concerning the degree of electronic interaction between the metal-containing subunits. For the specific case of the μ-2,3-dpp ligand, metal–metal coupling is considered "weak" by Fuchs et al.[16] and by Petersen and co-workers[22] and "strong" by Kalyanasundaram and Nazeeruddin.[27] This apparent contradiction derives from the parameters chosen to estimate the interaction. As pointed out recently,[13] the degree of interaction between metal-containing subunits of an oligometallic complex may be judged on the basis of the following experimental data: (i) differences in the first potential for the reduction of the bridging ligand between mononuclear and oligonuclear complexes; (ii) spectral shifts in metal → bridging ligand transitions between mononuclear and oligonuclear complexes; (iii) differences in the first potential for oxidation of the metals between mononuclear and oligonuclear complexes; (iv) differences between the first and the second potential for oxidation of the metals in an oligonuclear complex (which is related to the comproportionation constant). (i) and (ii) reflect the stabilization of the bridging π^*_{BL} orbitals, and (iii) and (iv) reflect stabilization of the π_{M} metal orbitals upon coordination of a second metal to the bridging ligand. Clearly, π^*_{BL} stabilization is a first-order effect and is always sizable,[56] whereas π_{M} stabilization is a second-order, much weaker effect, which is present only with truly delocalizing bridges. Our results illustrate these points well and show the important role played by the nonbridging ligands. Thus, from mononuclear to oligonuclear complexes, shifts in the first reduction potential of the bridging ligand (Table II, Figures 7 and 8) and in the Ru → BL CT bands (Table I, Figures 3 and 4) are always substantial, whereas differences in the first oxidation potentials of mono- and oligonuclear

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(56) An exception among the aromatic-type bridges is the anion of 3,5-bis(pyridin-2-yl)-1,2,4-triazole.[30]

species and, particularly, differences between the first and second oxidation potentials in oligonuclear complexes are small or even unnoticeable. This is particularly true when L = biq, since in such cases the π_M orbitals are already stabilized by the nonbridging ligand. In fact, the calculated values[57] of the comproportionation constants are 7×10^2 for complexes **5** and **8**, which only contain bpy as peripheral ligands, and 1×10^2 or smaller for the mixed bpy–biq complexes **7** and **10** and for the all-biq complexes **6** and **9**.

Conclusions

The mono-, di-, tri-, and tetrametallic complexes of general formulas $\mathrm{RuL_2(BL)^{2+}}$, $\mathrm{L_2Ru(\mu\text{-}BL)RuL_2^{4+}}$, $\mathrm{LRu[(\mu\text{-}BL)RuL_2]_2^{6+}}$, and $\mathrm{Ru[(\mu\text{-}BL)RuL_2]_3^{8+}}$ (L = bpy or biq; BL = 2,3- or 2,5-dpp) exhibit very intense absorption bands in the UV and visible regions, relatively long-lived luminescence both in a rigid matrix at 77 K and in fluid solution at room temperature, and a very rich electrochemical behavior. The electrochemical, spectroscopic, and photophysical properties of this family of complexes can be rationalized on the basis of metal- and ligand-centered redox orbitals and ligand-centered and metal-to-ligand charge-transfer excited states. Such properties can be tuned by a suitable choice of L, BL, and number of metal ions. Because of these properties, the complexes examined are good candidates for light absorption and/or light emission sensitizers,[37,58] as well as for luminescent probes and photochemical cleavers of DNA.[59,60]

The oligonuclear complexes can reversibly exchange a large number of electrons. For example, **13** can be reversibly reduced by nine electrons in the potential window −0.47/−1.79 V. The interaction between equivalent redox centers of the same complex is often too small to split the oxidation or reduction waves (for example, the three peripheral Ru ions of **15** and **16** are oxidized at the same potential). Because of their redox properties, these oligometallic complexes may be promising catalysts for multielectron-transfer processes, but the stability of the oxidized and reduced forms should first be verified and could pose problems.[16,22,27]

Corrected excitation spectra show that all the states populated by excitation in the visible region undergo conversion to the lowest (luminescent) excited state with the same (presumably unitary) efficiency. This property and the very high extinction coefficients all over the visible region exhibited by the tri- and tetrametallic complexes suggest that these species can be very efficient antenna devices,[61] for example for photoinduced electron or hole injection into semiconductors.[62-64]

It should be pointed out that for each complex replacement of a chelating ligand with a bridging BL ligand gives rise to a new complex that can be used as a "ligand" for the design of larger supramolecular species.[32] This "complexes as ligands" strategy based on components that exhibit the desired properties leads to a simple preparation of photochemical molecular devices[61] and more generally can be viewed as a structure-directed synthesis[65] to obtain new molecule-controlled materials. By such a "complexes as ligands" strategy, we have recently prepared[36] the heptametallic complex $\mathrm{Ru[(\mu\text{-}2,3\text{-}dpp)(bpy)Ru(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_3^{14+}}$ and we plan to design other homo- and heterooligometallic species of great theoretical and applicative interest.

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Supplementary Material Available: Tables of analytical, conductivity, and IR data (2 pages). Ordering information is given on any current masthead page.

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