

Contribution from Dipartimento di Chimica "G. Ciamician" dell'Università and Istituto Frae-CNR, Bologna, Italy, and Institute of Inorganic Chemistry, University of Fribourg, Fribourg, Switzerland

Absorption Spectra, Luminescence Properties, and Electrochemical Behavior of Tris-Heteroleptic Ruthenium(II) Polypyridine Complexes

Alberto Juris,^{*,1a,b} Sebastiano Campagna,^{1a,c} Vincenzo Balzani,^{*,1a,b} Gabriel Gremaud,^{1d} and Alex von Zelewsky^{1d}

Received February 3, 1988

The absorption spectra, luminescence properties (spectra, lifetimes, quantum yields), and electrochemical behavior of a series of nine Ru(II) complexes containing three different ligands are reported. The complexes examined are Ru(bpy)(biq)(L)²⁺, where bpy is 2,2'-bipyridine, biq is 2,2'-biquinoline, and L is one of the following ligands: Me₂-bpy (4,4'-dimethyl-2,2'-bipyridine), phen (1,10-phenanthroline), pq ((2-pyridyl)-2-quinoline), *i*-biq (3,3'-bisquinoline), pzpm ((2-pyrimidyl)-1-pyrazole), biimH₂ (2,2'-biimidazole), bpm (2,2'-bipyrimidine), taphen (dipyrido[3,2-*c*:2',3'-*e*]pyridazine), and dinapy (5,6-dihydrodipyrido[2,3-*b*:3,2-*i*]-1,10-phenanthroline). The absorption spectra are extremely rich because of the presence of three types of ligand-centered and three types of metal-to-ligand charge-transfer (MLCT) bands. The luminescence properties are very simple because in all cases only the lowest lying MLCT triplet is responsible for the emission. The cyclic voltammograms between +1.8 and -2.0 V show a reversible oxidation wave, attributed to metal oxidation, and three reversible reduction waves, attributed to successive reductions of the three different ligands. Extensive use of comparisons with the spectroscopic and electrochemical properties of the parent homoleptic and bis-heteroleptic complexes is made to arrive at specific assignments of absorption bands and redox waves. The results obtained confirm the extraordinary ability of the Ru(II)-polypyridine family to supply members with tunable properties and represent a further step toward the design of photosensitizers having the desired ground- and excited-state properties.

Introduction

In the last 10 years Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine) has attracted the attention of many research workers because of a unique combination of chemical stability, redox potentials, light absorption, luminescence emission, excited-state energy, and excited-state lifetime.²⁻⁸ Studies concerning this and other ruthenium(II) polypyridine complexes have made an important contribution to the growth of several branches of chemistry (photochemistry, photophysics, photocatalysts, electrochemistry, chemiluminescence) and to a better understanding of fundamental chemical processes (energy transfer, electron transfer).

An important aspect of the studies concerning the Ru(II)-polypyridine family is the possibility to change gradually (i.e., "to tune") the various ground- and excited-state properties by a judicious choice and combination of the ligands. A recent review article⁸ has shown that more than 200 bidentate polypyridine ligands (L) have been used in Ru(II) chemistry and that a great number of homoleptic Ru(L)₃²⁺ complexes have been prepared, covering a wide range of values of redox potentials, excited-state energies, excited-state lifetime, etc. Further possibilities for tuning are offered, of course, by the synthetic accessibility of bis-heteroleptic Ru(L)₂(L')₂²⁺ and tris-heteroleptic Ru(L)(L')(L'')²⁺ complexes. While many bis-heteroleptic complexes have already been prepared and studied,⁸ only very few and partial investigations on spectroscopic and electrochemical properties have concerned the Ru(L)(L')(L'')²⁺ species.⁹⁻¹¹ We wish to report results concerning absorption spectra, luminescence properties, and electrochemical behavior of a series of nine Ru(L)(L')(L'')²⁺ complexes recently synthesized in our laboratories.¹¹ The L, L', L'' polypyridine ligands contained in the complexes examined are shown in Figure 1.

Experimental Section

The preparation, characterization, and purification of the complexes examined (which are listed in Table I) are reported elsewhere.¹¹

Spectroscopic data, emission lifetimes, and emission quantum yields were obtained as previously described.¹² Ru(bpy)₃²⁺ in aerated aqueous solution was used as a quantum yield standard, assuming a value of 0.028.¹³

Electrochemical measurements were carried out in acetonitrile (AN) solution at room temperature with the equipment described in ref 12. The redox potentials of Ru(bpy)₃²⁺ under the same experimental conditions were used as secondary reference for the redox potentials of the new complexes. Half-wave potentials were calculated as an average of the cathodic and anodic peak potentials. The reported values are vs SCE. The criteria for reversibility were the separation between cathodic and anodic peaks (~60 mV) and the equal intensities of the cathodic and anodic currents.

Results

All the complexes examined were thermally stable in the solvents used for at least 20 h, as indicated by the constancy of their absorption spectra. Spectral changes, however, were observed upon light excitation leading to the replacement of the sterically demanding biq ligand by solvent molecules.¹¹

The absorption spectra of the nine complexes in acetonitrile solution at room temperature show a great number of bands. The full spectra of Ru(bpy)(biq)(*i*-biq)²⁺, Ru(bpy)(biq)(pzpm)²⁺, and Ru(bpy)(biq)(biimH₂)²⁺ are shown, as typical examples, in Figure 2. The wavelength and extinction coefficient of the lowest energy absorption maximum are gathered in Table I.

All the complexes examined exhibit luminescence both in a MeOH/EtOH rigid matrix at 77 K and in acetonitrile solution at room temperature. In all cases there is only one emission band, which shows some evidence of vibrational structure at 77 K. At room temperature the vibrational structure disappears, the half-width increases, and the emission maximum is red-shifted by 400-500 cm⁻¹. The wavelengths of the emission maxima at 77 and 300 K are shown in Table I.

The luminescence decay was strictly exponential in all cases. The lifetimes of the luminescent excited states at 77 and 300 K have been gathered in Table I, where also the room-temperature quantum yield values are reported.

The corrected excitation spectrum of Ru(bpy)(biq)(*i*-biq)²⁺ was recorded at room temperature (λ_{em} = 766 nm) and was found to be identical with the absorption spectrum.

The cyclic voltammograms in AN solution between +1.8 and -2.0 V vs SCE showed one reversible oxidation wave and three reversible reduction waves in all cases with the exception of Ru(bpy)(biq)(biimH₂)²⁺, which exhibited a reversible oxidation wave but an irreversible and somewhat irreproducible behavior

- (1) (a) University of Bologna. (b) Istituto FRAE-CNR. (c) Permanent address: University of Messina. (d) University of Fribourg.
- (2) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717.
- (3) DeArmond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* **1981**, *36*, 325.
- (4) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.
- (5) Waits, R. J. *J. Chem. Educ.* **1983**, *60*, 834.
- (6) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984; Chapter 15.
- (7) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.
- (8) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
- (9) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613.
- (10) Thummel, R. P.; Lefoulon, F.; Chirayil, S. *Inorg. Chem.* **1987**, *26*, 3072.
- (11) Gremaud, G.; von Zelewsky, A., submitted for publication in *Helv. Chim. Acta*.

- (12) Juris, A.; Belser, P.; Barigelletti, F.; von Zelewsky, A.; Balzani, V. *Inorg. Chem.* **1986**, *25*, 256.
- (13) Nakamaru, K. *Bull. Chem. Soc. Jpn* **1982**, *55*, 2697.

Table I. Spectroscopic and Electrochemical Results of Tris-Heteroleptic Ru(II) Complexes^a

complex	293 K				77 K ^b		293 K				
	λ_{abs} , nm (ϵ)	λ_{em} , nm	τ , μs	Φ^c	λ_{em} , nm	τ , μs	E_{ox} , ^d mV	E_{red} , ^d mV			
a	Ru(bpy)(biq)(Me ₂ -bpy) ²⁺	532 (9300)	765	0.25	0.008	732	1.49	1300	-920	-1390	-1720
b	Ru(bpy)(biq)(phen) ²⁺	525 (9500)	745	0.36	0.015	715	1.92	1350	-900	-1380	-1680
c	Ru(bpy)(biq)(pq) ²⁺	530 (9100)	742	0.23	0.008	715	2.56	1390	-880	-1190	-1620
d	Ru(bpy)(biq)(i-biq) ²⁺	533 (9200)	762	0.33	0.008	734	1.18	1290	-920	-1390	-1660
e	Ru(bpy)(biq)(pzpm) ²⁺	510 (7900)	728	0.41	0.012	702	2.75	1420	-890	-1380	-1650
f	Ru(bpy)(biq)(biimH ₂) ²⁺	552 (8900)	810	0.11	<0.002	778	0.81	1090	irrev		
g	Ru(bpy)(biq)(bpm) ²⁺	518 (7600)	727	0.45	0.014	702	2.09	1460	-820	-1100	-1560
h	Ru(bpy)(biq)(taphen) ²⁺	520 (9200)	724	0.38	0.014	702	2.17	1460	-650	-1000	-1510
i	Ru(bpy)(biq)(dinapy) ²⁺	580 (5800)	842	0.14	<0.002	807	0.55	1270	-660	-990	-1710

^aIn acetonitrile unless otherwise noted. ^bIn methanol/ethanol (4:1). ^cEstimated error <10%. ^dEstimated error 10 mV.

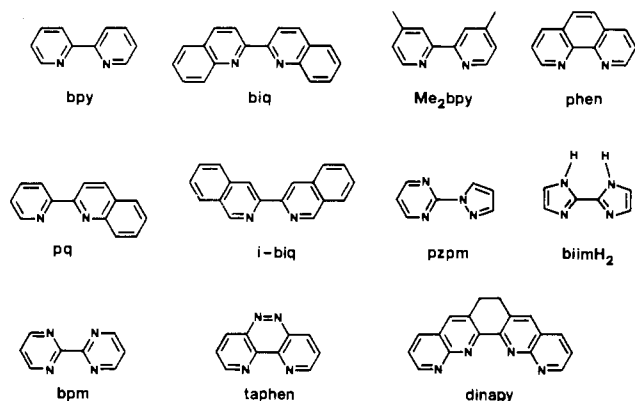
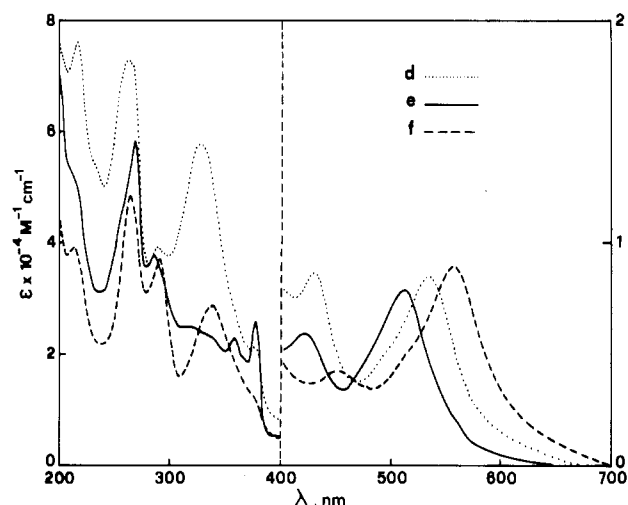


Figure 1. Structural formulas of the ligands.

Figure 2. Absorption spectra of Ru(bpy)(biq)(L)²⁺ complexes: d, L = *i*-biq; e, L = pzpm; f, L = biimH₂.

on reduction. It can be noted that irreversible and nonreproducible reduction waves were observed for Ru(bpy)₂(biimH₂)²⁺ by Haga and were attributed to the presence of traces of water in the solvent.¹⁴ The $E_{1/2}$ values of the various waves of the complexes studied are shown in Table I.

Discussion

The absorption, emission, and electrochemical properties of transition-metal complexes are usually discussed on the basis of a localized configuration model,^{15,16} i.e. assuming that each spectroscopic or redox state can be described in a sufficiently approximate way by a localized electronic configuration. In this approach, the electronic transitions and excited states of coor-

dination compounds can be classified as metal centered (MC), ligand centered (LC), and charge transfer (CT), either ligand to metal, LMCT, or metal to ligand, MLCT,¹⁵ and the redox processes can be classified as metal or ligand centered.¹⁶ Extensive studies carried out in the last 10 years have shown that such an approximate treatment is appropriate and most useful for the family of ruthenium(II) polypyridine complexes.^{8,16} For tris-heteroleptic Ru(L)(L')(L'')²⁺ complexes containing ligands that exhibit sufficiently different chromophoric and redox properties, an extremely rich spectroscopic and electrochemical behavior is expected: there are, in fact, seven types of orbitally different excited states (MC, MLCT, ML'CT, ML''CT, LC, L'C, and L''C) and four different types of redox orbitals (M, L, L', and L''). The assignment of the absorption bands, emission bands, and redox waves of the tris-heteroleptic complexes may be based on the available data concerning the homoleptic Ru(L)₃²⁺ and bis-heteroleptic Ru(bpy)₂(L)²⁺ complexes. For several purposes, the latter complexes are better models because of the constancy of the electronic properties and steric crowding of the Ru(bpy)₂ units.

Absorption Spectra. Comparison among the spectra of the tris-heteroleptic complexes (see, e.g., Figure 2) with the previously reported spectra of the available parent homoleptic Ru(L)₃²⁺ and bis-heteroleptic Ru(bpy)₂(L)²⁺ complexes⁸ leads to the following observations.

(i) The energy positions to the LC bands of each ligand are substantially unaffected by the other ligands. For example, the bpy bands at 266 and 286 nm, the biq bands at 358 and 377 nm, the *i*-biq band at 326 nm, and the taphen bands at 310 and 318 nm can be clearly identified in the Ru(bpy)(biq)(L)²⁺ complexes with L = *i*-biq (Figure 3) or taphen. Whether or not the extinction coefficients of those bands change from complex to complex is difficult to say because of partial overlap with bands of other ligands.

(ii) For each complex, only two maxima are present in the region of the charge-transfer bands since there is some overlap among the three types of CT bands, as expected from the positions of the CT bands in the parent homoleptic complexes.^{8,10,12,16-22} For Ru(bpy)(biq)(*i*-biq)²⁺ the energy separation of the three bands is large (for the homoleptic parent complexes, $\Delta E \sim 3400 \text{ cm}^{-1}$ for the CT bands involving *i*-biq and bpy and $\sim 3000 \text{ cm}^{-1}$ for the CT bands involving bpy and biq). In the tris-heteroleptic complex, however, the Ru \rightarrow *i*-biq CT band, expected around 390 nm, is hidden by the intense intraligand biq band with a maximum at 377 nm.

(iii) From the absorption spectra^{8,12,14,16-22} of the available Ru(L)₃²⁺ or Ru(bpy)₂(L)²⁺ parent complexes, one expects the

- (14) Haga, M.-A. *Inorg. Chim. Acta* **1983**, *75*, 29.
 (15) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic: London, 1970.
 (16) Ohsawa, Y.; Hanck, K. W.; DeArmond, M. K. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *175*, 229.

- (17) Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1980**, *63*, 1675.
 (18) Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582.
 (19) Juris, A.; Barigelletti, F.; Balzani, V.; Belser, P.; von Zelewsky, A. *Inorg. Chem.* **1985**, *24*, 202.
 (20) Bernhard, P.; Lehmann, H.; Ludi, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1216.
 (21) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617.
 (22) Belser, P.; von Zelewsky, A.; Juris, A.; Barigelletti, F.; Balzani, V. *Chem. Phys. Lett.* **1982**, *89*, 101.

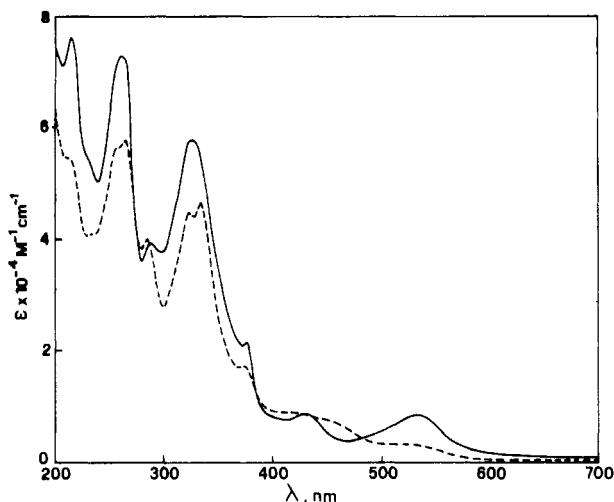


Figure 3. Comparison between the absorption spectrum of Ru(bpy)(biq)(i-biq)²⁺ (—) and the spectrum expected by averaging the extinction coefficients of the three homoleptic parent complexes (---).

following order of decreasing energy for the MLCT bands: *i*-biq \approx biimH₂ > taphen > phen \approx bpy \approx Me₂-bpy > bpm \approx pq > biq > dinapy. For L = pzpm, parent spectral data are not available, but judging from the reduction potentials (Table I), there seems to be no doubt that pzpm precedes biq in the above series. It follows that, except for that of Ru(bpy)(biq)(dinapy)²⁺, the lowest energy absorption band is the Ru → biq band. The results obtained show that the maximum of this band moves in the range 511–544 nm (19 600–18 100 cm⁻¹), indicating that there are ligand–ligand interactions. This is also evident from the values of the extinction coefficients. Figure 3 compares the absorption spectrum of Ru(bpy)(biq)(i-biq)²⁺ with that obtained from the summation of the extinction coefficients of the three homoleptic parent compounds divided by 3. One can see that the experimental spectrum exhibits extinction coefficients noticeably larger in the region of the Ru → biq CT band and noticeably smaller in the region of the Ru → bpy and Ru → *i*-biq bands. A similar behavior was previously observed by comparing the spectra of the bis-heteroleptic complexes containing bpy (or bpy type) and biq (or biq type) ligands with the spectra of their homoleptic parents.^{17,23} It seems likely that the changes in energy and extinction coefficient are caused both by the electronic properties of the other ligands, which modify the effective charge of the metal, and by the difference in the steric demand of bpy-type and biq-type ligands, which causes, for example, an increase in the Ru–bpy bond length in going from Ru(bpy)₃²⁺ to Ru(bpy)₂(biq)²⁺ or Ru(bpy)(biq)(i-biq)²⁺ and a decrease in the Ru–biq bond length in going from Ru(biq)₃²⁺ to the same mixed-ligand complexes. Since the energies and intensities of the CT bands are related to orbital overlap, changes in the extinction coefficients on changing metal–ligand bond distances are in fact expected.

Luminescence. The presence, with a few exceptions,^{24,25} of only one luminescence band due to emission from the lowest excited state confirms that in Ru(II) polypyridine complexes there are fast deactivation channels that convert upper excited states to the lowest one. The identity between absorption and excitation spectra for Ru(bpy)(biq)(i-biq)²⁺ shows that the intramolecular deactivation processes of the upper states to the luminescent one are \sim 100% efficient, at least in this complex. The luminescence lifetimes and quantum yields are in the expected range for MLCT emission of ruthenium(II) polypyridine complexes.⁸ The luminescent lifetime at 77 K roughly decreases with decreasing excited-state energy, as expected on the basis of the energy gap rule.⁷ The radiative rate constants at room temperature, obtained from the luminescence lifetime and quantum yield, have values in the

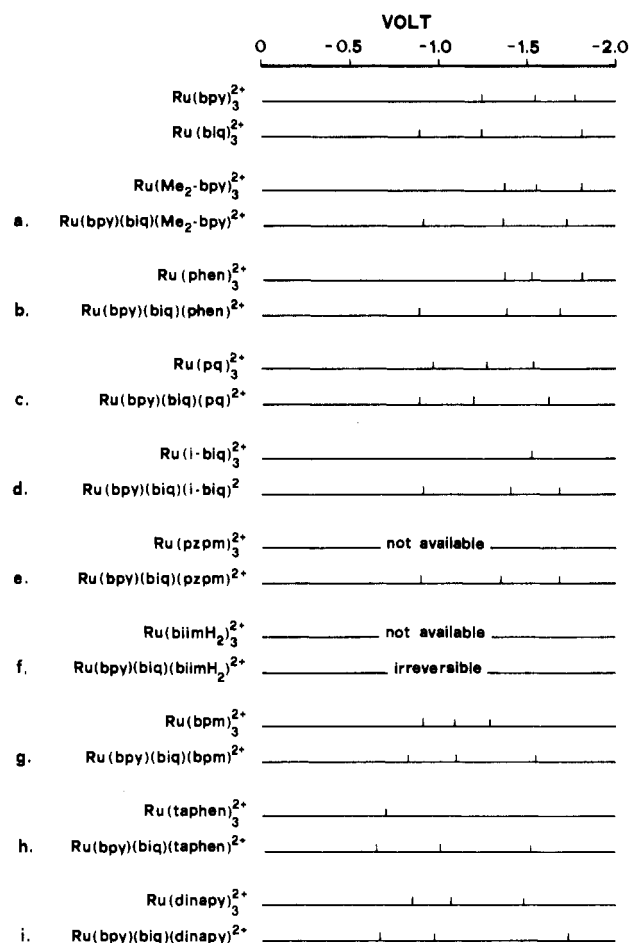


Figure 4. Schematic comparison of the reduction potentials for the Ru(bpy)(biq)(L)²⁺ complexes and their homoleptic parents.

range 2×10^4 – 4×10^4 s⁻¹, typical for ruthenium polypyridine complexes. The red shift of the emission maximum and the decrease of the luminescence lifetime in going from 77 K to room temperature are characteristic of MLCT excited states, as previously discussed by several authors.⁸

Comparison with the available emission spectra of the parent homoleptic and bis-heteroleptic complexes^{8,12,16,21,22,26} clearly shows that the emitting excited state involves the biq ligand for the Ru(bpy)(biq)(L)²⁺ complexes with L = Me₂-bpy, phen, pq, *i*-biq, pzpm, bpm, and taphen. For L = biimH₂, no parent data are available concerning luminescence. For Ru(bpy)(biq)(dinapy)²⁺, the lowest excited state involves the dinapy ligand, in agreement with expectations based on the spectroscopic and electrochemical properties of the parent Ru(bpy)₂(biq)²⁺, Ru(bpy)(dinapy)²⁺, Ru(biq)₃²⁺, and Ru(dinapy)₃²⁺ complexes.^{10,27} It is interesting to note that the energy of the emitting Ru → biq CT excited state and, as a consequence, the dynamic properties that determine its emission lifetime and quantum yield are modulated by the other ligands. Again, it seems likely that this modulation results from both electronic properties of the various ligands, which modify the effective charge of the metal, and the steric requirements, which may cause changes in the metal–biq bond lengths.

Electrochemistry. The electrochemical behavior of the Ru(bpy)(biq)(L)²⁺ complexes is qualitatively similar to that exhibited by other previously studied ruthenium(II) polypyridine complexes:^{3,8,18,28} an oxidation wave involving metal oxidation and a series of three reduction waves involving ligand reduction. Comparison with the available reduction potentials of the parent

(23) Thummel, R. P.; Decloitre, Y. *Inorg. Chim. Acta* **1987**, *128*, 245.

(24) Sullivan, B. P.; Abruna, H.; Finklea, H. D.; Salmon, D. J.; Nagle, J. K.; Meyer, T. J.; Sprintschnik, H. *Chem. Phys. Lett.* **1978**, *58*, 389.

(25) Blakley, R. L.; DeArmond, M. K. *J. Am. Chem. Soc.* **1987**, *109*, 4895.

(26) Kawanishi, Y.; Kitamura, N.; Kim, Y.; Tazuke, S. *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)* **1984**, *78*, 212.

(27) Juris, A.; Barigelletti, F.; Balzani, V.; Belser, P.; von Zelewsky, A. *Isr. J. Chem.* **1982**, *22*, 87.

(28) Vlcek, A. A. *Coord. Chem. Rev.* **1982**, *43*, 39.

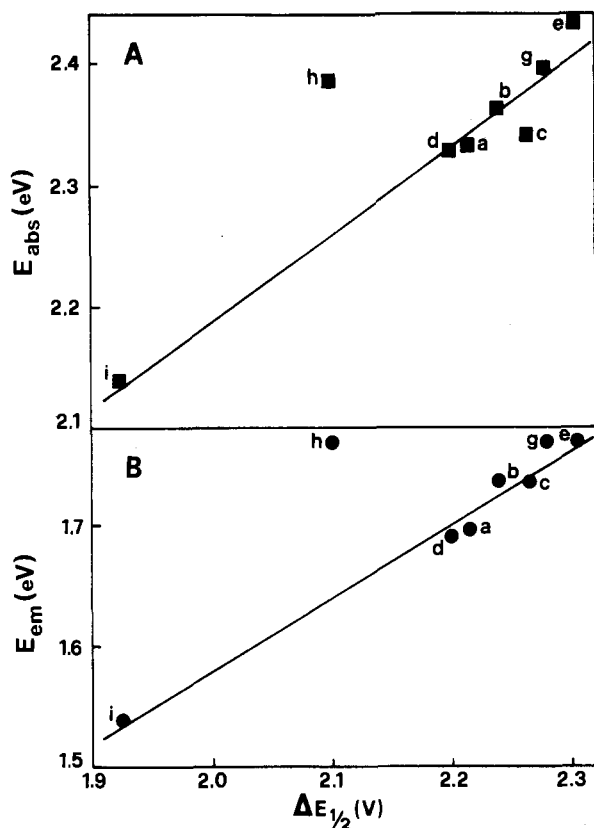


Figure 5. Correlations of the energies of the lowest MLCT absorption (A) and emission (B) bands with $\Delta E_{1/2}$ for the $\text{Ru}(\text{bpy})(\text{biq})(\text{L})^{2+}$ complexes. The complexes are labeled as in Table I. Leaving aside the point concerning $\text{Ru}(\text{bpy})(\text{biq})(\text{taphen})^{2+}$ (point h), the best fitting lines have correlation coefficients 0.97 (A) and 0.99 (B) and slopes 0.71 (A) and 0.61 (B).

homoleptic^{8,10,12,16-22} (Figure 4) and bis-heteroleptic^{8,10,12,14,16,17,19,21,29} complexes is most useful for a detailed assignment of the various reduction waves to specific ligands. For $\text{L} = \text{DM-bpy}$ and when there is no problem: the first reduction wave involves biq, the second wave bpy, and the third one L. For $\text{L} = \text{pq}$, the reduction order is biq, pq, and bpy. For $\text{L} = i\text{-biq}$, there is no problem for the first (biq) and the second (bpy) waves. The third wave may be a second reduction of biq or a first reduction of $i\text{-biq}$. For $\text{L} = \text{pzpm}$, parent data are not available. However, from the correlation between spectroscopic and electrochemical quantities (vide infra), there is no doubt that the first ligand to be reduced is biq. For $\text{L} = \text{biimH}_2$, clear results were not obtained but from the first reduction potential (-1.66 mV vs SCE) of $\text{Ru}(\text{bpy})_2(\text{biimH}_2)^{2+}$ it is known that biimH₂ is more difficult to reduce than bpy.¹⁴ Therefore, the first ligand to be reduced in $\text{Ru}(\text{bpy})(\text{biq})(\text{biimH}_2)^{2+}$ should be biq. For $\text{L} = \text{bpm}$, the order of the reduction waves is probably biq, bpm, bpy. Taphen is a very particular ligand, since it possesses a low-energy π^* orbital mainly localized on the peripheric nitrogens not related to the high-intensity $\text{Ru} \rightarrow \text{taphen}$ CT absorption.³⁰ The most likely reduction order for $\text{Ru}(\text{bpy})(\text{biq})(\text{taphen})^{2+}$ is taphen, biq, bpy. Judging from the parent complexes,^{10,27} dinapy is easier to reduce than biq, so that for $\text{L} = \text{dinapy}$ the order should be dinapy, biq, bpy.

DeArmond and co-workers^{3,31} and others²⁸ have pointed out that in ruthenium(II) polypyridine complexes the π^* orbital involved in the first reduction process is the same as that involved in the MLCT absorption and emission processes. Therefore, a linear correlation can be expected^{8,12,16,21,32-34} between the energy of the absorption (or emission) maximum and the quantity $\Delta E_{1/2} = [E_{1/2}(\text{RuL}_3^{3+/2+}) - E_{1/2}(\text{RuL}_3^{2+/+})]$, which is a measure of the energy difference between the HOMO and the LUMO orbitals. Such a correlation is obeyed by a number of ruthenium(II) polypyridine complexes, but $\text{Ru}(\text{taphen})_3^{2+}$ is known to be an exception.¹² Figure 5 shows the E_{abs} vs $\Delta E_{1/2}$ and E_{em} vs $\Delta E_{1/2}$ plots for the $\text{Ru}(\text{bpy})(\text{biq})(\text{L})^{2+}$ complexes. It is clear that the correlations are not obeyed for $\text{L} = \text{taphen}$. For such a complex both the lowest absorption band and the emission band apparently involve states at higher energy than expected from the π^* orbital involved in the reduction. This is in agreement with absorption and emission involving biq, whereas reduction involves the previously mentioned π^* taphen orbital mainly localized on the peripherical nitrogens. Why emission occurs from the higher biq-involving CT state rather than from the lowest CT state involving taphen is unclear, as are other peculiar properties of other taphen-containing complexes.^{12,30}

Conclusion

The tris-heteroleptic ruthenium(II) polypyridine complexes studied in this paper exhibit quite interesting absorption spectra and electrochemical behavior, as expected because of the presence of seven types of orbitally different excited states (MC, MLCT, ML'CT, ML''CT, LC, L'C, and L''C) and four different types of redox orbitals (M, L, L', and L''). The emission properties (spectra, lifetime, quantum yields) are much simpler in that they reflect the nature of the lowest triplet MLCT state, which, except in one case, involves the biq ligand. The absorption, emission, and redox data clearly show that there are ligand-ligand interactions originating from both electronic perturbations mainly transmitted through (and mediated by) the metal and steric requirements of some ligand such as biq. The results obtained confirm the extraordinary ability of the $\text{Ru}(\text{II})$ -polypyridine family to supply members with tunable properties and represent a further step toward the design of photosensitizers having the desired ground- and excited-state properties.

Acknowledgment. We thank G. Gubellini and V. Cacciari for technical assistance. This work was supported by the Progetto Strategico CNR "Processi di Trasferimento Monoelettronico", by the Ministero della Pubblica Istruzione, and by the Swiss National Science Foundation.

Registry No. $\text{Ru}(\text{bpy})(\text{biq})(\text{Me}_2\text{bpy})^{2+}$, 106588-07-2; $\text{Ru}(\text{bpy})(\text{biq})(\text{Me}_2\text{bpy})^{3+}$, 116209-98-4; $\text{Ru}(\text{bpy})(\text{biq})(\text{Me}_2\text{bpy})^+$, 116209-90-6; $\text{Ru}(\text{bpy})(\text{biq})(\text{phen})^{2+}$, 116209-82-6; $\text{Ru}(\text{bpy})(\text{biq})(\text{phen})^{3+}$, 116231-33-5; $\text{Ru}(\text{bpy})(\text{biq})(\text{phen})^+$, 116209-91-7; $\text{Ru}(\text{bpy})(\text{biq})(\text{pq})^{2+}$, 116209-83-7; $\text{Ru}(\text{bpy})(\text{biq})(\text{pq})^{3+}$, 116209-99-5; $\text{Ru}(\text{bpy})(\text{biq})(\text{pq})^+$, 116209-92-8; $\text{Ru}(\text{bpy})(\text{biq})(i\text{-biq})^{2+}$, 116209-84-8; $\text{Ru}(\text{bpy})(\text{biq})(i\text{-biq})^{3+}$, 116210-00-5; $\text{Ru}(\text{bpy})(\text{biq})(i\text{-biq})^+$, 116209-93-9; $\text{Ru}(\text{bpy})(\text{biq})(\text{pzpm})^{2+}$, 116209-85-9; $\text{Ru}(\text{bpy})(\text{biq})(\text{pzpm})^{3+}$, 116263-22-0; $\text{Ru}(\text{bpy})(\text{biq})(\text{pzpm})^+$, 116209-94-0; $\text{Ru}(\text{bpy})(\text{biq})(\text{biimH}_2)^{2+}$, 116209-86-0; $\text{Ru}(\text{bpy})(\text{biq})(\text{biimH}_2)^{3+}$, 116210-01-6; $\text{Ru}(\text{bpy})(\text{biq})(\text{bpm})^{2+}$, 116209-87-1; $\text{Ru}(\text{bpy})(\text{biq})(\text{bpm})^{3+}$, 116210-02-7; $\text{Ru}(\text{bpy})(\text{biq})(\text{bpm})^+$, 116209-95-1; $\text{Ru}(\text{bpy})(\text{biq})(\text{taphen})^{2+}$, 116209-88-2; $\text{Ru}(\text{bpy})(\text{biq})(\text{taphen})^{3+}$, 116210-03-8; $\text{Ru}(\text{bpy})(\text{biq})(\text{taphen})^+$, 116209-96-2; $\text{Ru}(\text{bpy})(\text{biq})(\text{dinapy})^{2+}$, 116209-89-3; $\text{Ru}(\text{bpy})(\text{biq})(\text{dinapy})^{3+}$, 116210-04-9; $\text{Ru}(\text{bpy})(\text{biq})(\text{dinapy})^+$, 116209-97-3.

(29) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444.

(30) Barigelletti, F.; Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. J. *Phys. Chem.* **1986**, *90*, 5190.

(31) Morris, D. E.; Ohsawa, Y.; Segers, D. P.; DeArmond, M. K.; Hanck, K. W. *Inorg. Chem.* **1984**, *23*, 3010.

(32) Ghosh, P.; Chakravorty, A. *Inorg. Chem.* **1984**, *23*, 2242.

(33) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1986**, *124*, 152.

(34) Barigelletti, F.; Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 4115.