

195. Spectroscopic, Electrochemical, and Kinetic Characterization of New Ruthenium(II) Tris-chelates Containing Five-Membered Heterocyclic Moieties

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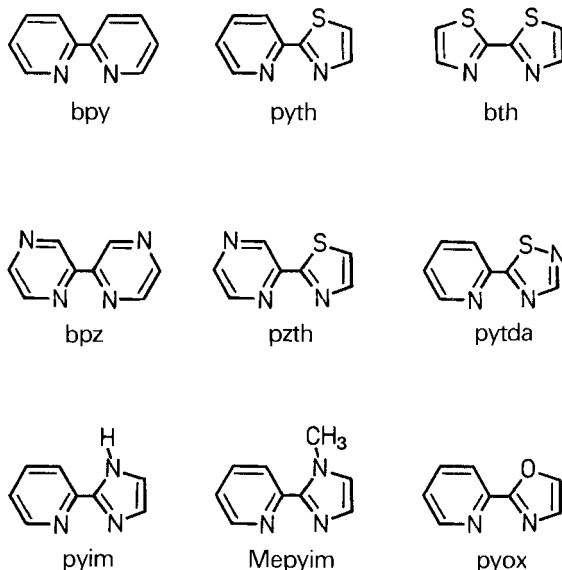
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Synthesis, redox, photophysical, and photochemical properties of $\text{Ru}(\text{NN})_3^{2+}$ complexes $\text{NN} = 2\text{-}((2'\text{-pyridyl})\text{thiazole (pyth), } 2\text{-}(2'\text{-pyrazyl})\text{thiazole (pzth), } 2,2'\text{-bithiazole (bth), } 5\text{-}(2'\text{-pyridyl})\text{-}1,2,4\text{-thiadiazole (pytda), } 2\text{-}(2'\text{-pyridyl})\text{imidazole (pyim), } 1\text{-methyl-}2\text{-}(2'\text{-pyridyl})\text{imidazole (Mepyim), and } 2\text{-}(2'\text{-pyridyl})\text{oxazole (pyox)}$) are described. Oxidation potentials for the $\text{Ru}^{3+/2+}$ couples in MeCN varied from about 0.80 V to 1.60 V vs. NHE. Three reduction waves were observed in all the cases except for $\text{Ru}(\text{pyim})_3^{2+}$ and $\text{Ru}(\text{Mepyim})_3^{2+}$ complexes and assigned to the one-electron reduction of each bidentate ligand. Absorption spectra contained bands in the UV (280–325 nm) and VIS (437–481 nm) regions which have been assigned to ligand-centered $\pi\text{-}\pi^*$ and metal-to-ligand charge-transfer $d\pi\text{-}\pi^*$ transitions, respectively. Emission spectra at 77 K were determined for all the complexes presenting maxima in the 580–650-nm region, with vibrational progression in some of them. Only pyth, pzth, bth, and pytda tris-chelates showed luminescence at room temperature in aqueous solution, with quantum yields ranging from 0.0013 to 0.0095 and excited-state lifetimes from 55 to 390 ns, as determined from pulsed laser techniques. Their E_{0-0} spectroscopic energies have been estimated from emission wavelength maxima at 77 K which, in turn, have allowed calculation of excited-state redox potentials. A plot of E_{0-0} vs. ΔE_{ν_s} , where $\Delta E_{\nu_s} = E_{\nu_s}(3+/2+) - E_{\nu_s}(2+/-)$, was linear with a slope of ca. 1.1 and a correlation coefficient of 0.999, demonstrating an identical nature of the orbital involved in spectroscopic and electrochemical processes. Photochemical properties of $\text{Ru}(\text{NN})_3^{2+}$ complexes have been tested using methyl viologen (MV^{2+}) in Ar-purged aqueous solution at pH 5. Stern-Volmer treatment has led to the determination of bimolecular quenching constants (0.5 to $2 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$) which parallel electron-transfer free-energy changes. Homogeneous back-reaction of primarily produced $\text{MV}^{+\cdot}$ and $\text{Ru}(\text{NN})_3^{3+}$ has been measured resulting to be slightly higher than diffusion control and independent of ligand nature. Rate constants for the scavenging of $\text{Ru}(\text{NN})_3^{3+}$ by added edta have been also determined (1.7 to $8.2 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$). Under such conditions, net production of $\text{MV}^{+\cdot}$ is attained with quantum yields varying from 0.003 to 0.038 (single-shot laser results).

Introduction. – Ruthenium(II) polypyridyl complexes have been widely studied because of their unusual properties as electron-transfer catalysts in photo-induced processes. $\text{Ru}(\text{bpy})_3^{2+}$ ($\text{bpy} = 2,2'\text{-bipyridine}$) has been taken as a model compound for such studies, and a huge amount of information about its ground and excited states has been gathered in the last ten years [1]. To tune its excited-state properties, a number of modifications in the basic structure of the bpy ligand have been tested, most of them preserving the six-membered moieties of the ligand and introducing two N-atoms [2], substituents [3], benzo-annellated rings [4], or aliphatic chains linking the rings [5].

However, there are only a few reports on the use of five-membered heterocycles as ligands for Ru(II) [6]. This fact has led us to a systematic investigation on this type of

ruthenium chelates, where the nature, number, and position of heteroatoms in the five-membered rings have been varied. Ligands selected for our study are depicted below. Tris-complexes of Ru(II) with 2,2'-bipyridine (bpy), 2-(2'-pyridyl)thiazole (pyth), 2,2'-bi-thiazole (bth), 2-(2'-pyrazyl)thiazole (pzth), 5-(2'-pyridyl)-1,2,4-thiadiazole (pytda), 2-(2'-pyridyl)imidazole (pyim), 1-methyl-2-(2'-pyridyl)imidazole (Mepyim), and 2-(2'-pyridyl)-oxazole (pyox) have been synthesized. The structure of 2,2'-bipyrazine ligand (bpz) has also been included for the sake of completion, but the corresponding data have been taken from the literature.



The aim of our study has been the comparison of photophysical and photochemical properties of complexes containing five-membered heterocyclic ligands with those of chelates including only six-membered moieties, and the rationalization of the behavior of the former.

Static characterization of the new complexes includes absorption and emission parameters and electrochemical data. Photokinetic characterization has been performed by using laser photolysis techniques on a ternary system photosensitizer/quencher/sacrificial agent, constituted by the $\text{Ru}(\text{NN})_3^{2+}$ complex (NN = heterocyclic chelating ligand), 1,1'-dimethyl-4,4'-bipyridinium dichloride (methyl viologen, MV^{2+}), and the disodium salt of ethylenediaminetetraacetic acid ($\text{Na}_2\text{H}_2\text{edta}$). Such a model system has been widely investigated in connection with solar-light-induced H_2O -photoreduction processes [7].

Results and Discussion. – *Electrochemical Data.* Oxidation and reduction half-wave potentials (*vs.* NHE) for the ground state of $\text{Ru}(\text{NN})_3^{2+}$ complexes are summarized in *Table 1*. These have been determined by cyclic voltammetry in MeCN solutions by reference to the $\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}$ oxidation peak (+1.260 V *vs.* NHE [5a]). For all the complexes, the single-electron-transfer electrodic processes have resulted to be reversible

Table 1. Half-Wave Potentials for Ru(NN)₃²⁺ Complexes^{a)} b)

Complex	Oxidation $E_{1/2}$	Reductions			$E_{1/2}^{3+/2+^{c)}$	$E_{1/2}^{2+^{c)}$
		$E_{1/2}$ (1)	$E_{1/2}$ (2)	$E_{1/2}$ (3)		
Ru(bpy) ₃ ²⁺	+1.26 ^{d)}	-1.35	-1.53	-1.78	-0.88	+0.79
Ru(pyth) ₃ ²⁺	+1.30	-1.22	-1.40	-1.66	-0.74	+0.82
Ru(bth) ₃ ²⁺	+1.33	-1.08	-1.27	-1.54	-0.59	+0.84
Ru(bpz) ₃ ^{2+e)}	+1.97	-0.69	-0.88	-1.15	-0.21	+1.49
Ru(pzth) ₃ ²⁺	+1.63	-0.88	-1.06	-1.35	-0.40	+1.15
Ru(pytda) ₃ ²⁺	+1.53	-0.88	-1.05	-1.25	-0.44	+1.09
Ru(pyim) ₃ ²⁺	+0.85	^{f)}			-1.30	
Ru(Mepyim) ₃ ²⁺	+0.83	-1.75	-1.95		-1.29	+0.37
Ru(pyox) ₃ ²⁺	+1.27	-1.33	-1.54	-1.80	-0.86	+0.80

^{a)} In V vs. NHE. Estimated error ± 0.01 V.

^{b)} Conditions: 5.0×10^{-4} M solns. in MeCN containing 0.1 M Bu₄NPF₆; Ar-purged; 293 ± 2 K.

^{c)} Calculated from corresponding ground-state potentials and 0–0 spectroscopic energies in eV (emission maxima at 77 K from Table 2, see text) [18].

^{d)} [5a].

^{e)} Values taken from [2e] and referred to NHE.

^{f)} No reduction waves present.

or quasireversible as it appears from the plot of anodic and cathodic peak separation (ΔE_p) vs. the square root of the sweep rate for each wave [4h]. One oxidation and three reduction waves are observed in every case except for pyim and Mepyim tris-chelates. No reduction waves were obtained for the Ru(pyim)₃Cl₂ complex, whereas two reduction waves are observed for the Mepyim complex above the solvent barrier limit.

Oxidation of Ru(II) polypyridine complexes is known to involve the $\pi(t_{2g})$ metal orbitals [8]. The values reported in Table 1 show that sequential replacement of py moieties by thiazole rings produces only a *ca.* +0.03 V constant increment from the Ru(bpy)₃²⁺ oxidation potential. This fact demonstrates that the $\pi(t_{2g})$ metal orbitals should have almost the same energy within the family of bpy, pyth, bth complexes. Conversely, a strong increase (*ca.* +0.30 V), also constant, is observed when pyrazine units are replaced by thiazole rings. This effect should be due to a larger interaction (*i.e.* back-donation) between the $\pi(t_{2g})$ metal orbitals and the π^* ligand orbitals for the pyrazine moieties which causes a gradual stabilization of the former orbitals along the bth, pzth, bpz series of complexes (Fig. 1). Similarly, since the oxidation potential reported for Ru(2,2'-biimidazole)₃²⁺ complex is +0.44 V (*vs.* NHE) [9], it should be concluded that sequential replacement of py by imidazole or *N*-methylimidazole units in each ligand decreases back-donation, raising the energy of the $\pi(t_{2g})$ orbitals by *ca.* -0.4 V per replaced moiety. This behavior of the imidazole ring is related to its higher-lying π^* orbitals [10] compared to those of other five-membered heterocycles (thiazole, oxazole). The apparent independence of heterocyclic subunits with respect to the redox properties of the corresponding complexes is further confirmed by the identical oxidation potentials reported for Ru(bpy)₃²⁺ and Ru(py)₃²⁺ complexes [11].

On the other hand, Ru(NN)₃²⁺ reduction potentials are related to the energy of lowest-lying π^* orbitals of individual ligands [12]. Therefore, assuming that the electrochemical reduction is a ligand-localized process, variations in the observed half-wave reduction potentials (Table 1) should be closely dependent on the relative energies of

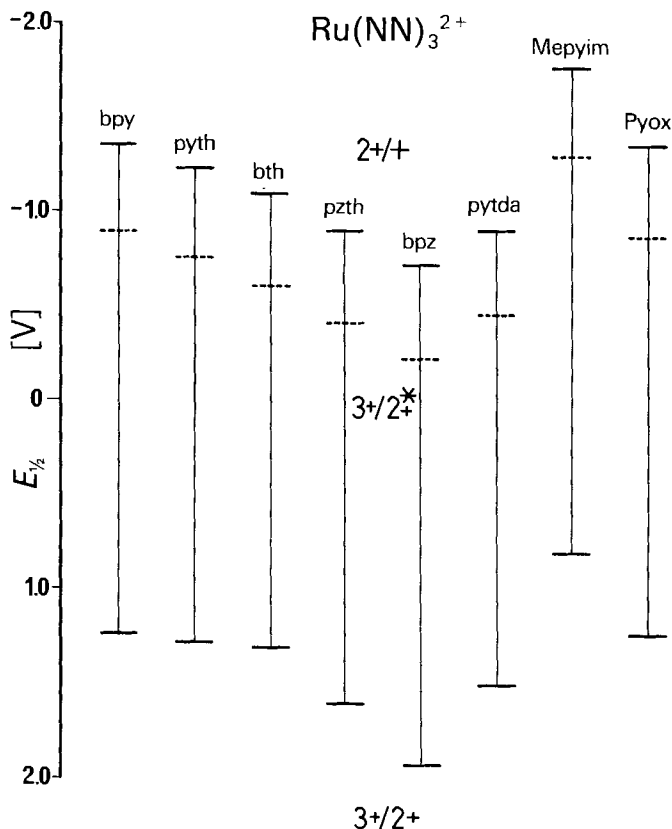


Fig. 1. Redox-potential diagram containing estimates of excited-state oxidation potentials based on the difference between the corresponding ground-state processes and the energy of 77-K emission maxima in eV

free-ligand π^* orbitals [4h, i]. As shown in Fig. 1, a constant modification in the reduction potentials occurs upon progressive substitution of a reference heterocyclic moiety by some other type of ring. The same observations are made for $E_{1/2}(1)$, $E_{1/2}(2)$, and $E_{1/2}(3)$ providing additional evidence of the ligand-localized model for electrochemical reduction of Ru(II) tris-chelates [13].

Spectroscopic Properties. The main absorption maxima and their corresponding absorption coefficients (in H_2O at 298 K), emission maxima, emission quantum yields, and excited-state lifetimes at 298 K (Ar-purged H_2O), as well as emission maxima at 77 K (EtOH/MeOH/4:1 v/v) are summarized in Table 2. Data for $\text{Ru}(\text{bpz})_3^{2+}$ complex [2d-f] are included for comparison. Spectroscopic parameters of $\text{Ru}(\text{NN})_3^{2+}$ complexes measured at 298 K (including excited-state lifetimes) resulted to be identical in pure aqueous and potassium-hydrogen-phthalate-buffered (0.05M, pH 5.0) solutions. Emission quantum yields were determined by using $\text{Ru}(\text{bpy})_3^{2+}$ as standard ($\Phi_{\text{em}} = 0.042 \pm 0.002$ for degassed aqueous solutions at room temperature [14]).

Complete absorption spectra for 2.0×10^{-5} M aqueous solutions of Ru(II) complexes are depicted in Figs. 2 and 3. All of the tris-chelates show intense absorption bands in the

Table 2. Spectroscopic Properties of Ru(NN)₃²⁺ Complexes

Complex	Absorption ^{a)}		Emission			
	298 K		298 K ^{b)}			77 K ^{c)}
	λ_{\max} [nm]	ϵ [M ⁻¹ cm ⁻¹]	λ_{\max} [nm]	Φ_{em}	τ_0 [ns]	λ_{\max} [nm]
Ru(bpy) ₃ ²⁺	285 (78 100)	452 (13 700)	613	0.042 ^{d)}	610	580
Ru(pyth) ₃ ²⁺	296 (51 500)	465 (14 700)	642	0.0061	217	609
Ru(bth) ₃ ²⁺	325 (40 900)	480 (17 400)	682	0.0014	113	647
Ru(bpz) ₃ ²⁺	294 (55 200)	441 (15 000) ^{e)}	603 ^{c)}	0.074 ^{f)}	1040 ^{g)}	570 ^{g)}
Ru(pzth) ₃ ²⁺	311 (47 000)	460 (17 000)	649	0.0095	390 ^{h)}	613
Ru(pytda) ₃ ²⁺	288 (48 000)	481 (12 100)	658	0.0013	55	630
Ru(pyim) ₃ ²⁺	292 (51 400)	439 (15 000)	i)			577
Ru(Mepyim) ₃ ²⁺	295 (47 100)	445 (15 200)	i)			587
Ru(pyox) ₃ ²⁺	280 (40 100)	437 (11 200)	i)			583

a) In H₂O solution.

b) In Ar-purged H₂O or potassium-hydrogen-phthalate buffer (0.05 M, pH 5) soln., uncorrected.

c) In EtOH/MeOH 4:1 soln., uncorrected.

d) [14].

e) [2d] [17].

f) [2e].

g) Adapted from [2f].

h) Excited-state lifetime is only 65 ns in pH 5.0 potassium-hydrogen-phthalate buffer (0.05 M).

i) No luminescence at 298 K.

UV region which can be clearly ascribed to ligand-centered $\pi-\pi^*$ transitions by comparison with absorption spectra of free ligands [1a]. In addition, the VIS region of the spectra is dominated by strong metal-to-ligand charge transfer (MLCT) absorptions, their profile and intensity being similar to those reported for other well characterized ruthenium complexes [1a].

Results displayed in Table 2 indicate that replacement of a py by a th moiety in the complexed ligand causes a progressive red shift of the MLCT band as well as an increase in the intensity of the absorption. Successive substitution of pyrazine rings of the bpz complex reveals the same trend. Introduction of a third heteroatom into the five-membered ring also produces a bathochromic shift but lowers significantly the intensity of the VIS absorption band. On the contrary, replacement of a S- by a N- or O-atom induces a blue shift in the MLCT absorption maximum (Ru(2,2'-biimidazole)₃²⁺ absorbs at 396 nm [9]). Energy variations of these $d\pi-\pi^*$ absorption bands within a given series of complexed ligands (bpy, pyth, bth; bpz, pzth, bth; bpy, pyim, bim) parallels the observed trends of reduction potentials (Table 1) as a result of the π^* orbital energy being involved in both quantities (*vide infra*).

As far as the emission spectra are concerned, all of the ruthenium chelates show a strong emission band of similar intensity at 77 K. No luminescence is observed at 298 K for complexes containing five-membered rings with heteroatoms different from sulfur. These results may be interpreted in terms of a higher probability of the deactivation of the ³MLCT state *via* thermal population of a metal-centered state (³MC) which in turn decays without emission [1a] [3e] [4f] [15]. In fact, this deactivation pathway must be very important for pyim, Mepyim, and pyox complexes as a result of a lower ³MLCT-³MC energy gap, since room-temperature emission from their ³MLCT states is not observed.

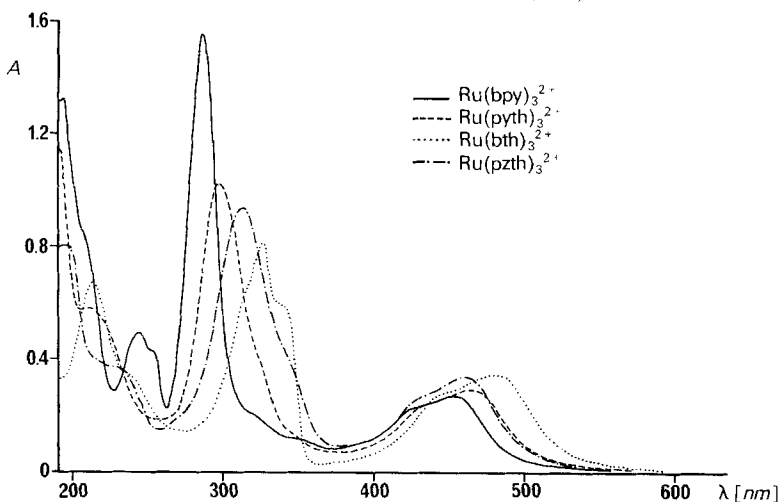


Fig. 2. UV/VIS spectra of $2.0 \cdot 10^{-5}$ M aq. solutions of Ru(II) tris-chelates with bpy, pyth, bth, and pzth ligands

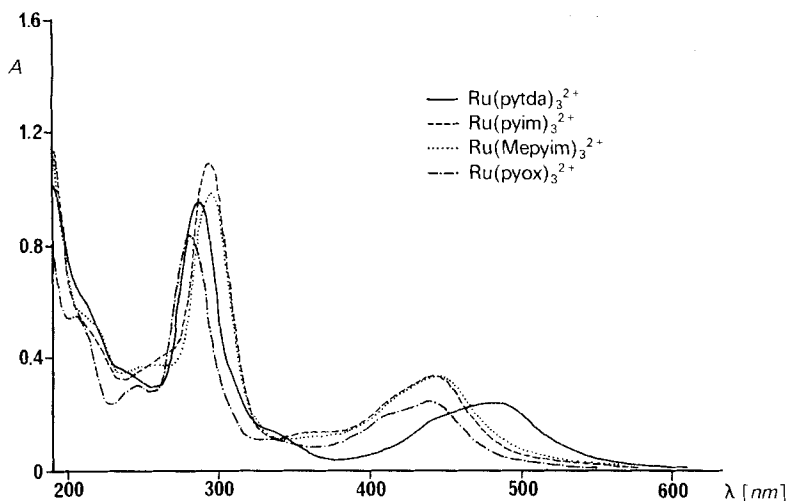


Fig. 3. UV/VIS spectra of $2.0 \cdot 10^{-5}$ M aq. solutions of Ru(II) tris-chelates with pytda, pyim, Mepyim, and pyox ligands

Likewise, for the same reason, complexes with S-containing five-membered heterocyclic moieties show lower emission quantum yields than $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpz})_3^{2+}$ (Table 2).

It is well established for metal chelates that a decrease of the energy of the metal-centered triplet state occurs, when the binding N–N angle providing optimal orbital overlap is modified, as a consequence of lowering the ligand-field strength [3c] [5c] [16]. Given the intrinsic geometry of the ligands containing five-membered heterocyclic rings, their larger binding angle should be one of the factors affecting differences in those energies when comparing our series of complexes to chelates only containing six-membered heterocycles. The corresponding variations in emission lifetimes (τ_0) are expected to have the same origin.

On the other hand, excited-state lifetimes are identical for H₂O and pH 5 potassium-hydrogen-phthalate solutions (Table 2). Ru(pzth)₃²⁺ is an exception for which a significant decrease of the lifetime has been observed at pH 5 (65 ns, compared to 390 ns in pure H₂O). Lever and coworkers [17] have reported a similar pH-dependent behavior of the bpz complex, which has been attributed to an enhanced basicity of the bpz ligand upon electronic excitation of the complex leading to protonation and, hence, diminution of the excited-state lifetime. Efficient quenching of the excited pzth complex occurs at pH 5, whereas for the bpz complex a higher acidity (ca. pH 2) is required in order to attain the same decrease in lifetime [17]. This is undoubtedly due to a larger basicity of the electronically excited state of the former, i.e. *[Ru^{III}(pzth)₂(pzth⁻)]²⁺ vs. the latter *[Ru^{III}(bpz)₂(bpz⁻)]²⁺.

Relation between Electrochemical and Spectroscopic Parameters. Emission wavelength maxima at 77 K allow an estimation of the E_{0-0} spectroscopic energy for the series of complexes [3e] [4i]. These values (in eV) have been used to calculate excited state redox potentials (Table 1) according to the equations [18]:

$$E_{\frac{1}{2}}^{3+/2+*} = E_{\frac{1}{2}}^{3+/2+} - E_{0-0}$$

$$E_{\frac{1}{2}}^{2+*/+} = E_{\frac{1}{2}}^{2+*/+} + E_{0-0}$$

Our data for Ru(bpy)₃²⁺ are in agreement with those previously reported [3e] [4i]. A good correlation between the difference of ground state redox potentials, $\Delta E_{\frac{1}{2}}$ ($\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}}^{3+/2+} - E_{\frac{1}{2}}^{2+*/+}$), and the energy corresponding to absorption or emission maxima

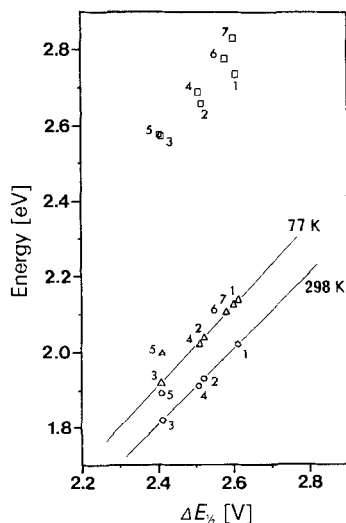


Fig. 4. Correlation of the HOMO-LUMO energy gap, determined by the emission energy at 77 K (Δ) or 298 K (\circ) in eV, and the difference between the ground-state redox potentials in V ($\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}}[\text{Ru}(\text{NN})_3]^{3+/2+} - E_{\frac{1}{2}}[\text{Ru}(\text{NN})_3]^{2+*/+}$). Least-squares linear fit for 77-K data yields a slope of 1.13 and an intercept of -0.80 eV (correlation coefficient 0.999), and a slope of 1.03 and an intercept of -0.66 eV (correlation coefficient 0.998) for 298-K data. Values of absorption energy in eV are also included for comparison with a linear fit yielding a correlation coefficient of only 0.936. Compounds: (1) Ru(bpy)₃²⁺; (2) Ru(pyth)₃²⁺; (3) Ru(bth)₃²⁺; (4) Ru(pzth)₃²⁺; (5) Ru(pytda)₃²⁺; (6) Ru(Me-pyim)₃²⁺; (7) Ru(pyox)₃²⁺.

has been reported for Ru(II) polypyridyl complexes [2e] [4h–i] [19]. These observations have been interpreted in terms of an identical nature of the orbital involved in the first electrochemical reduction (redox orbital) and the one implicated in the MLCT absorption and π^* -d emission (spectroscopic orbital). As one can see from *Fig. 4*, an excellent correlation between $\Delta E_{1/2}$ and emission data has been obtained for both, 77 K (six points, correlation coefficient 0.9990) and 298 K measurements (four points, correlation coefficient 0.9982), excluding pytda tris-chelate in both cases. The fact that a linear least-squares fit cannot easily be applied to absorption data does *not* have to be considered anomalous, since it would imply to assume an identical energy difference between the 1 MLCT state (primarily involved in the electronic transition following light absorption [1a]) and the 3 MLCT state for all the complexes.

The unity value of the slope of the linear fit using emission data confirms that spectroscopic and redox orbitals are equivalent. An intercept should arise from the different electronic configuration of the state produced by electrochemical reduction of the Ru(NN) $_3^{2+}$ complex, $(t_{2g})^6(\pi^*)^1$, and the spectroscopic excited state $(t_{2g})^5(\pi^*)^1$. In this way, coulombic factors providing a constant additive contribution, allow for a good correlation between both states.

The exclusion of the pytda complex from those correlations may be due to a different orbital nature of its π^* level involved in the electronic excitation and the LUMO implicated in the electrochemical reduction, as it has been emphasized for other ruthenium polypyridine complexes [4i].

Kinetic Behavior of the System Ru(NN) $_3^{2+}$ /MV $^{2+}$ /edta. Two alternative mechanisms have been reported for electron-transfer quenching of the excited state of ruthenium complexes containing chelate ligands, their efficiency depending on the particular redox potentials of the species involved in the deactivation process: $^*\text{Ru}(\text{NN})_3^{2+}$ and quencher (Q) [1] [20]. When 1,1'-dimethyl-4,4'-bipyridinium dichloride (MV $^{2+}$) is used as quencher, electron transfer occurs in most cases from the excited state of the complex *via* an oxidative mechanism [21]. However, reductive quenching processes of some $^*\text{Ru}(\text{NN})_3^{2+}$ have also been established [22]. For the three-component system, both mechanisms provide the regeneration of the sensitizer and a net accumulation of the reduced relay (MV $^{+ \cdot}$).

Ru(bpy) $_3^{2+}$ is one of the complexes, the excited state of which is oxidatively quenched by MV $^{2+}$ in the presence of edta as electron donor [23]. For the system Ru(NN) $_3^{2+}$ /MV $^{2+}$ /edta, this mechanism can be formulated in several steps:

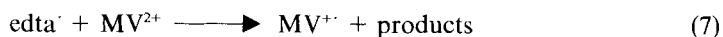
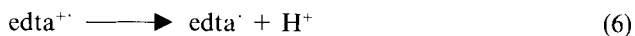
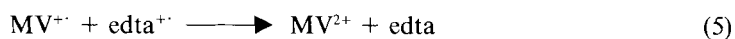
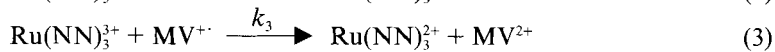
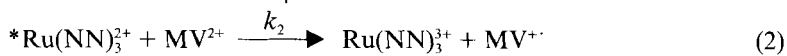
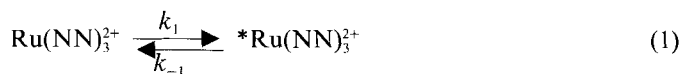


Table 3. Kinetic Parameters and Quantum Yields for the Systems $Ru(NN)_3^{2+}/MV^{2+}/edta^a)$

Complex	$10^{-6}k_{-1}^b)$ [s ⁻¹]	$10^{-9}k_2^c)$ [M ⁻¹ · s ⁻¹]	$10^{-10}k_3^e)$ [M ⁻¹ · s ⁻¹]	$10^{-8}k_4^f)$ [M ⁻¹ · s ⁻¹]	$\Phi_{MV^{2+}}(\phi_q)^g)$	$\Phi_{MV^{2+}}(\phi_q)^h)$
Ru(bpy) ₃ ²⁺	1.64 ± 0.02	1.60 ± 0.04 (-10.1)	1.0 ± 0.2 ⁱ⁾	1.7 ± 0.1	0.092 (0.96)	0.086 (0.75)
Ru(pyth) ₃ ²⁺	4.74 ± 0.05 ^{h)}	1.08 ± 0.02 (-6.9) ^{k)}	1.6 ± 0.3	4.0 ± 0.2	0.038 (0.85)	0.034 (0.75)
Ru(bth) ₃ ²⁺	8.85 ± 0.09	0.53 ± 0.01 (-3.5)	^{l)}	8.2 ± 0.4	0.010 (0.60)	0.013 (0.75)
Ru(pzth) ₃ ²⁺	15.4 ± 0.2	^{m)} (+0.9)			< 0.003	
	2.56 ± 0.03 ⁿ⁾	^{m)} ^{a)} (+0.9)			0.014 ⁿ⁾	
Ru(pytda) ₃ ²⁺	18.2 ± 0.2	2.18 ± 0.08 (0.0)	^{l)}	3.9 ± 0.3	0.003 (0.75)	0.003 (0.75)

- a) In Ar-purged aq. potassium-hydrogen-phthalate buffer (0.05 M, pH 5.0) solns., unless otherwise stated; [Ru(NN)₃²⁺] = 2.0 × 10⁻⁵ M. Kinetic constants refer to scheme depicted in the text.
- b) k_{-1} = 1/τ₀, measured in absence of MV²⁺ and edta.
- c) Bimolecular quenching constant determined from linear Stern-Volmer plots of τ₀/τ vs. [MV²⁺].
- d) In parenthesis, free-energy change of the quenching reaction ΔG_{et} in kcal · mol⁻¹, calculated according to [18]: ΔG_{et} = 23.06 [E(3+/2+*) - E(MV²⁺/MV⁺)] = -0.44 V vs. NHE, [1b].
- e) Homogeneous recombination constants determined at [MV²⁺] = 5.0 · 10⁻² M, in absence of edta.
- f) Rate constants for the scavenging of Ru(NN)₃²⁺ by edta calculated for pseudo-first-order conditions, [edta] = 5.0 × 10⁻² M at constant quenching efficiency (see g)).
- g) Quantum yield for MV⁺ production (for calculation, see [21a]) measured at constant [MV²⁺] = 2.5 · 10⁻² M, [edta] = 5.0 · 10⁻² M; precision ± 5%. In parenthesis, the quenching efficiency φ_q = k₂[MV²⁺]/(k₋₁ - k₂[MV²⁺]).
- h) Quantum yield for MV⁺ production determined at constant quenching efficiency.
- i) 5.1 · 10⁹ M⁻¹ · s⁻¹, when [MV²⁺] = 1.0 · 10⁻² M.
- j) 4.5 · 10⁶ s⁻¹ reported in [25].
- k) 5.2 · 10⁸ M⁻¹ · s⁻¹ (-6.7 kcal · mol⁻¹) reported in [25].
- l) Too low MV⁺ production to allow measurement.
- m) No quenching with MV²⁺ observed.
- n) In hydrogen-phosphate buffer (0.05 M, pH 7.0).

Kinetic results of investigated three component systems, containing our series of tris-chelates, MV⁺ and edta, are gathered in Table 3. Laser-photolysis experiments have been usually performed in pH 5, Ar-purged, aqueous potassium-hydrogen-phthalate (0.05M) solutions at room temperature. No quenching was observed for complexes lacking emission at 298 K (Table 2), even at high MV²⁺ concentration (0.1M).

Irradiation by a laser pulse is generating the excited state of the ruthenium complex which is consequently deactivated by unimolecular or bimolecular processes. Unimolecular deactivation rate constants (k₋₁) have been calculated from the lifetimes of the excited states (τ₀, Table 2); these lifetimes have been experimentally determined by monitoring the decay of the emission signal (λ_{max}^{em}, Table 2) in the absence of any quencher, followed by least-squares fitting to a first-order kinetic pattern. Variations observed for lifetimes within the series of complexes have been discussed above.

Rate constants of the bimolecular electron-transfer quenching by MV²⁺ (k₂) have been determined in the absence of edta by a Stern-Volmer experiment. In every case, a good linear fit (correlation coefficients > 0.998) was obtained for the plot of (τ₀/τ) - 1 vs. [MV²⁺]. Different ionic strenght of solutions or variation of the type of buffer used increase the difficulty of a quantitative comparison of the obtained results with those previously reported for Ru(bpy)₃²⁺ (5 · 10⁸ to 1.8 · 10⁹ M⁻¹ · s⁻¹) [23] [24] and Ru(pyth)₃²⁺ (3.2 · 10⁸ M⁻¹ · s⁻¹) [25].

As it appears from *Table 3*, a progressive decrease in k_2 occurs along the series of bpy, pyth, bth tris-complexes. This fact is due to an increase of the excited-state potentials of the implied complexes (*Table 1*) and, hence, to a diminution of the driving force of the electron-transfer process. Differences in free energies of the particular electron-transfer reactions (ΔG_{et} , reaction (2)), calculated from the redox potentials of the involved species, have been included in *Table 3*. A correlation between $\ln k_2$ and ΔG_{et} follows the *Rehm-Weller* [26] (or *Marcus* [27]) profile in the region of moderate negative ΔG_{et} values, as verified for $\text{Ru}(\text{bpy})_3^{2+}$ and other polypyridyl complexes by using a series of related quenchers [1d] [28].

It is remarkable that no quenching has been found for $\text{Ru}(\text{pzth})_3^{2+}$, neither at pH 5 nor at pH 7 (potassium-hydrogen-phthalate buffer). Whereas the first observation may be related to a competitive deactivation of the excited state by protonation of the complexed ligand, the second one reflects the lack of driving force for the electron-transfer quenching by MV^{2+} ($\Delta G_{\text{et}} = +0.9 \text{ kcal} \cdot \text{mol}^{-1}$). Since it has been established that in the presence of edta the quenching of the electronically excited state of $\text{Ru}(\text{bpz})_3^{2+}$ proceeds *via* a reductive mechanism, such a possibility was also tested for $^*\text{Ru}(\text{pzth})_3^{2+}$ at pH 5, but no change in the excited-state lifetime was observed for edta concentrations as high as 0.1 M.

The highest value of k_2 was obtained for the pytda complex. Although a small driving force is attributable to the oxidative quenching with MV^{2+} , some contribution of static quenching could probably explain the difference of rate constants, when compared with $\text{Ru}(\text{pyth})_3^{2+}$, taking into account the presence of an additional N-atom in the outer part of the five-membered moieties.

The rate constant of the back-transfer of the electron (k_3) between the primarily produced MV^{+} and $\text{Ru}(\text{NN})_3^{3+}$ species (in absence of edta) has been determined by monitoring the decay of the MV^{+} absorption at 602 nm [29] at the microsecond time scale, followed by a least-squares fit to a second-order kinetic pattern. An alternative monitoring of the bleaching recovery of the MLCT absorption of $\text{Ru}(\text{NN})_3^{2+}$ led to the same results. Good linear plots of $1/[\text{MV}^{+}]$ *vs.* time were obtained only for complexes yielding sufficiently high MV^{+} concentrations in order to allow for a quantitative analysis by its 602-nm absorption (*Table 3*). The difference between the published k_3 values for the $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$ system ($2.8 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ [23c]) and our result ($1.0 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$, $[\text{MV}^{2+}] = 5 \times 10^{-2} \text{ M}$) may be attributed to ionic strength effects as a consequence of the approximate *Debye-Brönsted* dependence of electron-transfer reactions [21b] [23a] [30], and also to the possibility of electron transfer taking place at large distances as discussed by *Rau et al.* [24b]. It should be noted that in reducing the MV^{2+} concentration to $1 \times 10^{-2} \text{ M}$, k_3 is diminished to a value of $5.0 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ (*Table 3*).

Furthermore, bimolecular rate constants for the scavenging of $\text{Ru}(\text{NN})_3^{2+}$ by edta (k_4) have been measured. This reaction allows for net production of MV^{+} by favorable competition of process (4) *vs.* back reaction (3). This constant has been redetermined for the $\text{Ru}(\text{bpy})_3^{2+}$ complex, since very different values have been reported for similar experimental conditions (10^6 to $10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$ [23a]). Our result (*Table 3*) agrees with the one reported by *Keller et al.* ($1.1 \cdot 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$ [23c]) where, in both cases, laser-photolysis techniques have been used.

As it appears from data in *Tables 1* and *3*, rate constants k_4 depend on the positive oxidation potential of $\text{Ru}(\text{NN})_3^{2+}$ and, hence, correspond within the given series of complexes to a progressive increase of the driving force of the process. The anomalous

low rate constant observed for the pytda complex could be related to a *Marcus*-type behavior [27] of this ground-state electron-transfer reaction involving edta. In accord to this hypothesis, a decrease of the reaction rate constant would be expected for sufficiently negative ΔG_{et} values (*Marcus* 'inverted' region).

Moreover, it is surprising that the electron-transfer reaction between the oppositely charged species ($\text{Ru}(\text{NN})_3^{3+}$ and edta, predominantly present in its trianionic form at pH 5 [31]), occurs at quite low rates, compared to those of processes involving positively charged species (e.g. reaction (3), Table 3). If some extent of ionic association between edta and $\text{Ru}(\text{NN})_3^{3+}$ is considered [23a], involving mainly the carboxylate groups of edta, then effective orbital overlap between the N-atoms of edta and the ruthenium complex is prevented and, thus, electron-transfer efficiency is lowered.

Finally, quantum yields of MV^{2+} production ($\Phi_{\text{MV}^{2+}}$) have also been measured by laser photolysis following the procedure reported in [21a] (Table 3). The coefficient correcting for reflections on cell walls has been redetermined (now $R = 0.95$), and a more recently published value of the molar absorption coefficient of MV^{2+} has been used ($13700 \text{ m}^{-1} \cdot \text{cm}^{-1}$ [29]). Given the fact that the actual quantum yield of MV^{2+} production depends on the MV^{2+} concentration, two series of experiments were carried out, the first using constant MV^{2+} and edta concentrations ($2.5 \cdot 10^{-2} \text{ M}$ and $5.0 \cdot 10^{-2} \text{ M}$, respectively), and the second keeping a constant quenching efficiency ($\phi_q = k_2[\text{MV}^{2+}]/(k_{-1} + k_2[\text{MV}^{2+}]) = 0.75$). The first series allows for quantum-yield determinations regardless the mechanism of quenching, whereas the second series tests the reactivity of ruthenium complexes towards electron transfer to MV^{2+} in order to generate MV^{+} .

The $\Phi_{\text{MV}^{2+}}$ found for $\text{Ru}(\text{bpy})_3^{2+}$ complex (at $\phi_q = 0.96$, Table 3) appears to be half of the value reported for similar conditions but obtained in continuous irradiation experiments [23a] [31]. This result can be explained taking into account that, under conditions of continuous irradiation, a second equivalent of MV^{2+} is produced by the slow non-photochemical reaction (7) [23a, c]. However, this is not a competitive process, when pulsed laser excitation is used. On the other hand, the observed production of MV^{2+} at pH 7 by the $\text{Ru}(\text{pzth})_3^{2+}$ complex, which is not oxidatively quenched by MV^{2+} , must be attributed to the reductive quenching mechanism occurring in the presence of edta.

A comparison between both series of experiments shows a direct correlation of quantum yields and corresponding quenching efficiencies. This fact responds to the equation $\Phi_{\text{MV}^{2+}} = \Phi_T \cdot \phi_q \cdot \phi_{ce}$ [23b], where Φ_T is the quantum yield of triplet-state formation and ϕ_{ce} is the solvent cage-escape efficiency of the primarily produced $\text{Ru}(\text{NN})_3^{3+}$ and MV^{+} species. A number of experiments in order to determine independently Φ_T and ϕ_{ce} are presently undertaken [32].

In conclusion, electrochemical, photophysical and photochemical characterizations of $\text{Ru}(\text{II})$ tris-chelates containing five-membered heterocyclic moieties have shown their ability to act as electron-transfer photosensitizers. Some modifications in the five-membered rings are now being investigated for an optimization of the photosensitized electron transfer process [33], and for a better understanding of the photophysical pathways involving $\text{Ru}(\text{II})$ heterocyclic complexes.

Experimental. – *Materials.* $\text{RuCl}_3 \cdot 3 \text{H}_2\text{O}$ (Fluka), 2,2'-bipyridine (Merck, p.a.), and 1,1'-dimethyl-4,4'-bipyridinium dichloride trihydrate (methyl viologen, Fluka) were used without further purification. Bu_4NPF_6 (Fluka) was purified twice by dissolution in hot acetone, filtration, and reprecipitation with H_2O ; the purified compound was then dried under vacuum at 70° . MeCN (Scharlau-Ferosa) was spectroquality grade and dried over 3-Å

molecular sieves for a week before electrochemical measurements. Abs. EtOH and MeOH were also spectroquality grade and used as received. H₂O was doubly distilled and passed through a *Millipore Milli-Q* purification train. All other reagents were anal. grade and used without further purification. Microanalyses were performed at the Centro de Investigación y Desarrollo (CSIC), Barcelona.

Synthesis of Compounds. The preparation of ligands will be reported in [34]. Ru(II) tris-complexes were prepared by adapting literature procedures, summarized in two general methods.

Method A [2e]. RuCl₃·3 H₂O (1 mmol) and a 20–50% excess over the stoichiometric amount of ligand required were dissolved in 15 ml of ethylene glycol. The mixture was heated at reflux temp. under N₂ for 1–3 h. The resulting soln. was cooled to r.t. and then filtered to remove possible metallic impurities. The filtrate was diluted with 25 ml of H₂O, and the tris-chelate was then precipitated by dropwise addition of sat. aq. NH₄PF₆ soln. The colored solid was collected by filtration, washed with abundant H₂O, and vacuum-dried at 70° for at least 48 h. Then, it was purified twice by dissolution in a small amount of MeCN (or an MeCN/acetone 1:1), filtration, and slow reprecipitation with Et₂O. Finally, the complexes were vacuum-dried at 70° for at least 24 h.

Method B [35]. Ca. 1 mmol of RuCl₃·3 H₂O and a 30% excess of ligand were dissolved in 30 ml of 95% EtOH and heated at reflux temp. under N₂ for 76 h. The resulting orange-red soln. was cooled to r.t. and filtered. The complex was then precipitated from the filtrate with sat. aq. ammonium hexafluorophosphate soln. The purification procedure was the same as given in *Method A*. If the chloride salt is required, the resulting hot soln. is concentrated by slow evaporation under N₂, and acetone is slowly added until complete precipitation of the complex is attained.

All the complexes were firstly characterized by microanalytical data and conductivity measurements (*Table 4*). In addition, structural and configurational elucidation was performed by ¹H- and ¹³C-NMR spectroscopy [36].

Equipment and Procedures. Absorption spectra were taken in aq. solns. at r.t. either with a *Perkin-Elmer Lambda-3*, equipped with a *Perkin-Elmer 3600 Data Station*, or with a *Shimadzu UV-260* spectrophotometer. Uncorrected emission spectra at 298 K (Ar-purged aq. solns.) were recorded using a *Perkin-Elmer MPF-44E* spectrofluorometer; excitation was carried out in the highest intensity absorption band of the VIS region. Emission quantum yields (excitation: 470 nm) were calculated in reference to published data for Ru(bpy)₃³⁺ (0.042 [14]) applying appropriate absorbance corrections [4h]. Low-temp. (77 K) uncorrected emission spectra were measured using a *Perkin-Elmer LS-5* spectrofluorometer equipped with a low-temperature accessory and the *3600 Data Station*. A mixture of EtOH/MeOH 4:1 was used as solvent yielding transparent glasses at 77 K.

Half-wave potentials were obtained in Ar-purged MeCN solns. (5.0·10⁻⁴ M) of the complexes by the cyclic voltammetry technique using a Pt-disk working electrode, a Ag/0.01M AgNO₃ (MeCN) reference electrode, and a Pt-wire counter electrode. Scan speed was 200 mV·s⁻¹ and 0.1M Bu₄NPF₆ was the supporting electrolyte. All the potentials were calculated in reference to the Ru(bpy)₃³⁺ oxidation peak (3+/2+, 1.260 V vs. NHE [5a]). The electrochemical equipment consisted of an *Amel 551* potentiostat, an *Amel 566* function generator, an *Amel 566* interface, and a *Hewlett-Packard 7035B X-Y* recorder. Conductivity measurements were performed in a *Metrohm*

Table 4. Reaction Conditions, Analytical and Conductivity Data for Ru(NN)₃²⁺ Complexes

Complex	Method	Reaction time [h]	Yield ^{a)} [%]	Found [%]				Calc. [%]				A _M ^{b)} c)	
				C	H	N	S	C	H	N	S		
Ru(bpy) ₃ (PF ₆) ₂	B	72	78										318 ^{d)} , 287 ^{e)}
Ru(pyth) ₃ (PF ₆) ₂	B	72	82	32.66	1.83	9.48	10.89	32.84	2.07	9.58	10.96		300 ^{d)}
Ru(bth) ₃ (PF ₆) ₂	A	3	98	23.99	1.13	9.10	21.97	24.13	1.35	9.38	21.48		294 ^{e)}
Ru(pzth) ₃ (PF ₆) ₂	A	1	95	28.87	1.50	14.13	10.97	28.64	1.72	14.32	10.92		292 ^{d)}
Ru(pytda) ₃ (PF ₆) ₂	A	3	94	29.26	1.57	14.33	11.09	28.64	1.72	14.32	10.92		265 ^{e)}
Ru(pyim) ₃ Cl ₂	B	72	71	47.71	3.72	20.10		47.45	3.48	20.75			29 ^{d)}
Ru(Mepyim) ₃ (PF ₆) ₂	A	1	98	36.88	2.93	14.32		37.37	3.13	14.51			281 ^{d)}
Ru(pyox) ₃ (PF ₆) ₂	B	72	98	34.37	1.97	9.89		34.75	2.19	10.13			296 ^{d)}

^{a)} Before purification.

^{b)} Molar conductivity of 5·10⁻⁴ M solns. in MeCN; estimated error ± 3%.

^{c)} Molar conductivity of 2:1 electrolytes in MeCN (ca. 10⁻³ M): 220–300 Ω⁻¹cm²mol⁻¹, [38]; anomalous value for pyim complex may be attributed to ionic association in MeCN soln.

^{d)} At (21 ± 0.5)°.

^{e)} At (16 ± 0.5)°.

E382 apparatus equipped with a EA660 thermostated cell. Data obtained for ca. $5 \cdot 10^{-4}$ M MeCN solns. of the complexes were compared with those published for 2:1 electrolytes [37].

Kinetic measurements and MV^{+} quantum yields were obtained with a laser-photolysis equipment. The excitation source was a frequency-doubled Nd-YAG laser (*JK Lasers System 2000*) providing 15 ns pulses at 532 nm with energies up to 50 mJ per pulse. The analyzer system was composed by a Xe lamp (450 W, *Oriel*), a grating monochromator (*Bausch & Lomb 33-86-76*), a photomultiplier (*Hamamatsu R-928*), and a *Tektronix R-7912* transient digitizer interfaced to a *Digital PDP 11/04* computer or, alternatively, a *Tektronix 7D20* digital oscilloscope coupled to a *Hewlett-Packard 87 XM* computer used also for kinetic analysis of the transient signals. Ar-purged $2.0 \cdot 10^{-5}$ M solns. of the ruthenium chelates were used in such experiments. H_2O , 0.05M potassium-hydrogen-phthalate (pH 5.0), or 0.05M potassium-hydrogen-phosphate (pH 7.0) buffers were used as solvents.

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