

Research Article

Synthesis, Characterization, and Photochemical Properties of a New Square Mn(I)-Ru(II) Complex Using Pyrazine as Bridge Ligand

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The photochemical properties of the complexes *cis, fac*-[Ru(phen)₂(pz)₂-Mn(CO)₃Br]₂⁴⁺ (I), *cis*-[Ru(phen)2(pz)₂]²⁺ (II), and *fac*-Mn(CO)₃(pz)₂Br (III) where phen is phenanthroline and pz is pyrazine in acetonitrile solution are reported. The three complexes were characterized using ¹H NMR, UV-vis and FTIR spectroscopy and electrochemical (cyclic voltammetry and spectroelectrochemical) techniques. The complexes show intense absorption in the visible region assigned to the population of MLCT excited states. The absorption spectrum of I is the sum of the spectra of the mononuclear species II and III, and the two oxidation potentials at +1.10 and +1.56 V versus Ag/AgCl observed in I are ascribed to the different coordination environments of metal centers. The photolysis in the acetonitrile solution resulted in the pz dissociation to give the monoacetonitrile complexes for I, II, and III, respectively.

1. Introduction

The investigation of spectroscopic, electrochemical, and photochemical properties of manganese compounds has attracted much attention due to the potential application of these compounds in the development of the supramolecular system which may work photochemically for clean energy sources in renewable solar fuels [1, 2]. Most of current research is being focused on the covalent coupling of a photoactive Ru(II) polypyridinic complex to a high-valence mono- and/or multinuclear μ -oxo bridged manganese complexes. Herein, we wish to report a novel, square pyrazine donor-acceptor complex, composed of a triscarbonyl manganese complex linked to two ruthenium(II) phenanthroline complexes via two pyrazine bridge ligands. Our approach, introducing three good π acceptor (CO) and one good π donor (Br⁻) ligand, was chosen because of the abilities of these ligands to accept and donate electronic density to

metal centers and in this way to stabilize the high oxidation states that the manganese center may acquire during the photoinduced electron transfer reaction. For this reason, in this work the photochemical stability of the complexes was studied.

2. Experimental

2.1. General. All synthesis and electrochemical and spectroscopic experiments were carried out under purified N₂ atmosphere, using Schlenk techniques. RuCl₃·xH₂O, 1,10'-phenanthroline (phen), pyrazine (pz), and lithium chloride were from Aldrich; tetrabutylammonium hexafluorophosphate (TBAPF₆) and bromide pentacarbonyl manganese from Strem. HPLC grade acetonitrile and dichloromethane were distilled prior to use. The solutions were carefully handled in the dark before the experiments were

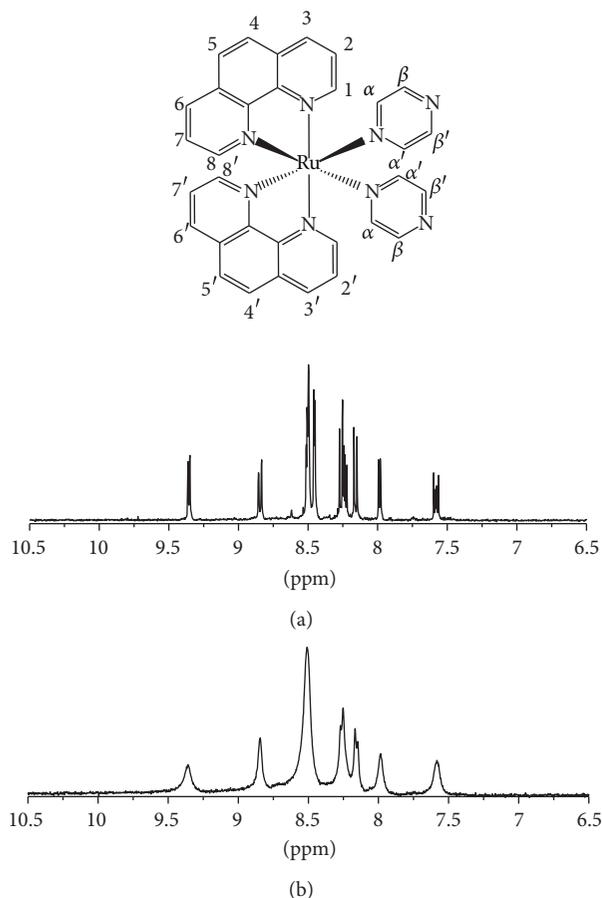


FIGURE 1: ^1H NMR spectra in CD_3CN of the aromatic region to the complex **II** (a) and complex **I** (b).

performed. The complexes $\text{cis-}[\text{Ru}(\text{phen})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ [3], $\text{cis-}[\text{Ru}(\text{phen})_2\text{CO}_3]\cdot 2\text{H}_2\text{O}$ [4], $\text{cis-}[\text{Ru}(\text{phen})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$ [5], and $[\text{Mn}(\text{CO})_3(\text{pz})_2\text{Br}]$ [6] were prepared by the literature routes. FTIR spectra were measured in CaF_2 windows in CH_2Cl_2 solution on a Bomem-Michelson 102 spectrometer in the $4000\text{--}1000\text{ cm}^{-1}$ region. UV-visible spectra were recorded on an HP-8453 A (Diode array) spectrophotometer. NMR spectra were recorded using a Bruker DRX400 spectrometer. All chemical shifts (δ) are given in ppm units with reference to the hydrogen signal of the methyl group of tetramethylsilane (TMS) as internal standard. Monochromatic irradiations at 350 nm and 420 nm were generated using an RMR-600 model Rayonet Photochemical reactor using RMR-3500 and RMR-4200 lamps, respectively. The continuous photolysis experiments were followed by UV-vis. Time-resolved optical spectra were obtained using a laser flash-photolysis apparatus containing a Continuum Q-switched Nd:YAG laser (Continuum, Santa Clara, CA) with excitation provided by the third harmonic at λ 355 nm. Cyclic voltammetry was performed using an μ Autolab Type III potentiostat. Voltammograms were obtained in CH_3CN (1 mM TBPf_6) at 22°C in a light-protected voltammetric cell with a platinum cylinder disc for both the working and the auxiliary electrodes. A silver wire

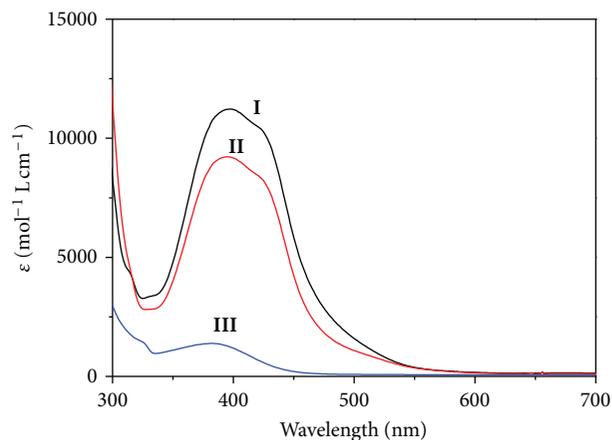


FIGURE 2: Electronic spectra in CH_3CN solution of **(I)** $\text{cis, fac-}[\text{Ru}(\text{phen})_2(\text{pz})_2\text{-Mn}(\text{CO})_3\text{Br}]_2$, **(II)** $\text{cis-}[\text{Ru}(\text{phen})_2(\text{pz})_2]$, **(III)** $\text{fac-}[\text{Mn}(\text{CO})_3(\text{pz})_2\text{Br}]$.

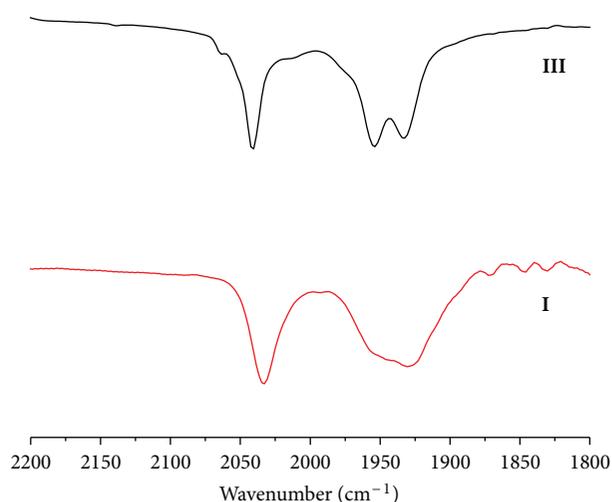


FIGURE 3: FTIR spectra of complexes **III** (black line) and **I** (red line) in CH_2Cl_2 at room temperature, with CaF_2 window.

coated with silver chloride was used as reference electrode, connected to the bulk of the solution by a Luggin capillary filled with the same solvent and electrolyte. Solutions were deoxygenated with a stream of N_2 and maintained under a positive pressure of N_2 during the measurements. The concentration of the complexes was kept always at 1 mM.

2.2. Synthesis

2.2.1. $\text{cis, fac-}[\text{Ru}(\text{phen})_2(\text{pz})_2\text{-Mn}(\text{CO})_3\text{Br}]_2(\text{PF}_6)_4$ (**I**). $\text{Mn}(\text{CO})_5\text{Br}$ (74 mg, 0.27 mmol) was dissolved in degassed acetone (50 mL), and the complex $\text{cis-}[\text{Ru}(\text{phen})_2(\text{pz})_2]$ (250 mg, 0.27 mmol) was added. It was stirred under dark for 12 hours at room temperature. The orange precipitate formed was filtrated and dried under vacuum. Yield = 80%.

2.2.2. $\text{cis-}[\text{Ru}(\text{phen})_2(\text{pz})_2](\text{PF}_6)_2$ (**II**). $[\text{Ru}(\text{phen})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ (200 mg, 0.35 mmol) and pyrazine (282 mg, 3.52 mmol) were

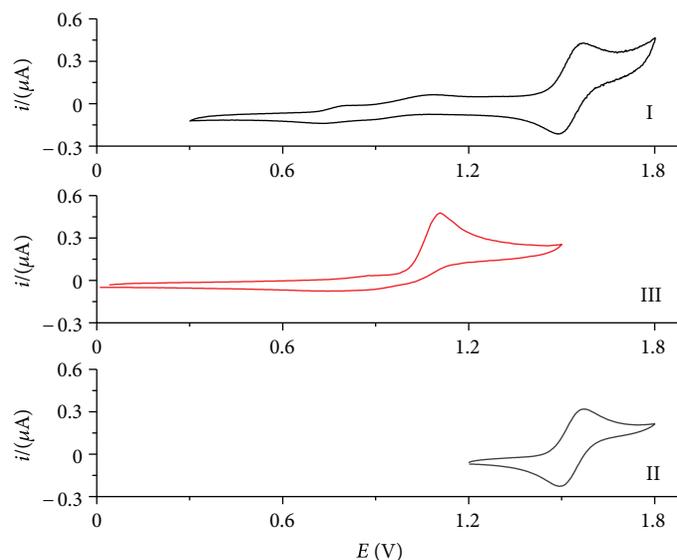


FIGURE 4: Cyclic voltammograms of complexes **I**, **II** and **III** (1 mM), TBPF₆ (0.1 M) versus Ag/AgCl, scan rate 100 mV/s, 25 °C, in CH₃CN.

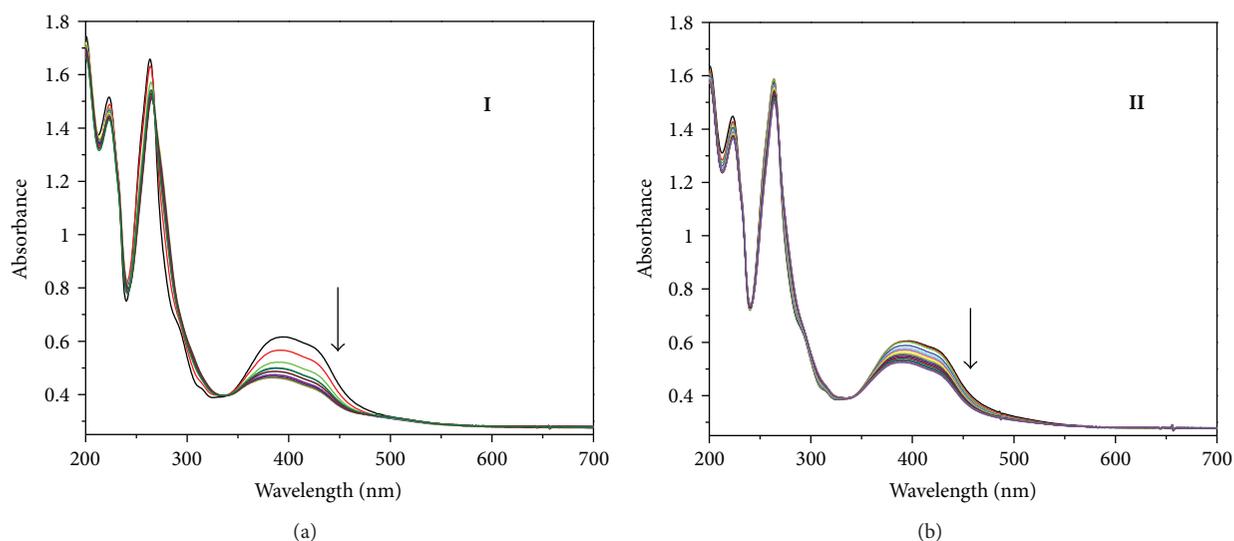


FIGURE 5: Spectroelectrochemical of complex **I** (1.5 mM in CH₃CN; 0.1 M TBAPF₆) and complex **II** (1.5 mM in CH₃CN; 0.1 M TBAPF₆) in an OTTLE cell, oxidation $E_{\text{applied}} = 1.5$ V versus Ag/AgCl.

refluxed in a 1 : 1 EtOH/H₂O solution for 6 hours. Upon cooling to room temperature, a saturated solution of ammonium hexafluorophosphate was added to the solution to precipitate an orange product, which was isolated by filtration. The orange solid was recrystallized using acetone/ether. Yield: 70%.

2.2.3. *fac*-[Mn(CO)₃(pz)₂Br](**III**). Mn(CO)₅Br (200 mg, 0.73 mmol) was dissolved in degassed CH₂Cl₂ (50 mL) and pyrazine (117 mg, 1.45 mmol). It was stirred under dark for 12 hours at room temperature. The yellow precipitate formed was filtrate and dried under vacuum. Yield: 80%.

3. Results and Discussion

The square complex was synthesized in a manner similar to a previously published procedure [1], starting from *cis*-[Ru(phen)₂(pz)₂]²⁺ and considering the complex Mn(CO)₅Br as a ligand (Scheme 1).

The ¹H NMR spectral data for the ligands and complexes in CD₃CN are listed in Table 1 using the numbering scheme as represented for complex **II** as follow. The signals of the complex **I** were assigned by comparison and analysis of the precursor Ru(phen)₂Cl₂ and the free pyrazine. In the complex **I**, the phenanthroline protons appeared as eight

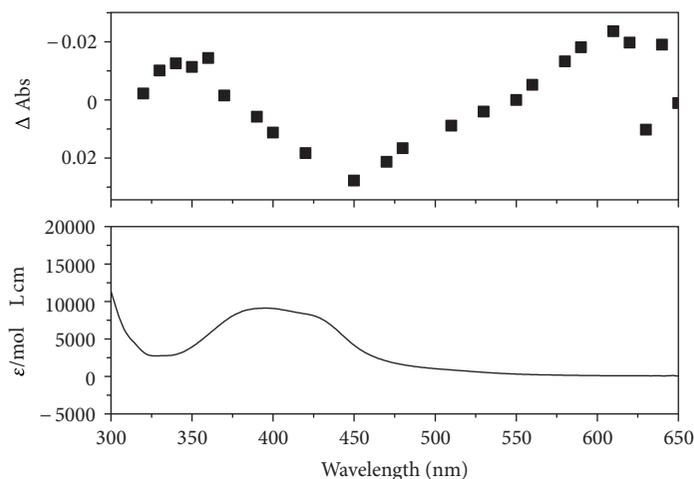
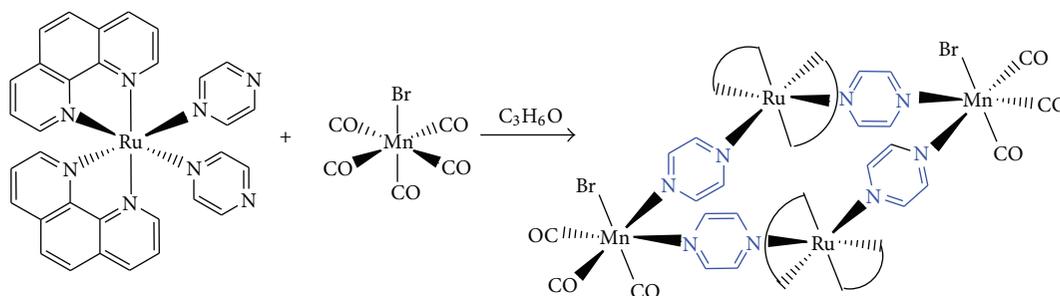


FIGURE 6: Transient (upper) and experimental (low) absorption spectra of complex I in acetonitrile.



SCHEME 1: Synthesis of square complex I.

TABLE 1: ^1H NMR spectral data of complexes I and II in CD_3CN .

δ_{H} (ppm)	Complex II	Complex I
Proton type		
$\text{H}_1 \text{H}_1'$	9.35 (2H, d)	9.35 (4H)
$\text{H}_2 \text{H}_2'$	8.25 (4H, m)	8.26 (8H)
$\text{H}_3 \text{H}_3'$	8.84 (2H, d)	8.84 (4H)
$\text{H}_4 \text{H}_4'$	8.25 (4H, m)	8.26 (8H)
$\text{H}_5 \text{H}_5'$	8.14 (2H, d)	8.15 (4H)
$\text{H}_6 \text{H}_6'$	8.50 (2H, d)	8.50 (4H)
$\text{H}_7 \text{H}_7'$	7.57 (2H, m)	7.58 (4H)
$\text{H}_8 \text{H}_8'$	7.98 (2H, dd)	7.98 (4H)
$\text{H}_\alpha \text{H}_\alpha'$	8.49 (4H, d)	8.50 (8H)
$\text{H}_\beta \text{H}_\beta'$	8.45 (4H, d)	8.50 (8H)

signals instead of four signals to the free ligand, as expected for the *cis* isomer. The two pyrazine α and β protons were observed at 8.49 (4H, d) and 8.45 (4H, d). On coordination of Ru(II) to Mn(I) (Figure 2, Table 1), the linewidth of all signals were broadened due to the presence of the bromide ion coordinated at the manganese center. The absence of new signals in the whole spectrum, as expected to a triangle complex, suggests the formation of the square complex, which was further confirmed by signals integration [7]. In the

TABLE 2: Electrochemistry properties of complexes I, II, and III in CH_3CN .

	$E_{\text{ox}}/E_{\text{red}}, V$	$\nu\text{CO cm}^{-1}$	$\lambda_{\text{max}}, \text{nm} (\epsilon)$
Complex I	1.10 0.79/0.73	2032, 1938	394 (11500); 442 (10400)
Complex II	1.56/1.49	—	394 (9100) 425 (8000)
Complex III	1.10 0.87/0.89	2041, 1953, 1932	381 (2900)

square complex, all the assignments were done using the same numbering figure as complex II, Figure 1.

3.1. Absorption Properties. The absorption spectra of complexes I, II, and III in CH_3CN solution are shown in Figure 2. The absorption maximum of 380 nm ($\epsilon_{\text{max}} = 1400 \text{ mol}^{-1} \text{ L cm}^{-1}$) for III appears as a shoulder on the strong $\pi\text{-}\pi^*$ absorption bands of the ligands, while the complex II exhibits the intense and broad MLCT absorption ($\lambda_{\text{max}} = 397 \text{ nm}$; $\epsilon_{\text{max}} = 9200 \text{ mol}^{-1} \text{ L cm}^{-1}$) typical of Ru^{II} polypyridine complexes [8]. The absorption spectrum of I ($\lambda_{\text{max}} = 397 \text{ nm}$; $\epsilon_{\text{max}} = 11230 \text{ mol}^{-1} \text{ L cm}^{-1}$) is consistent with the

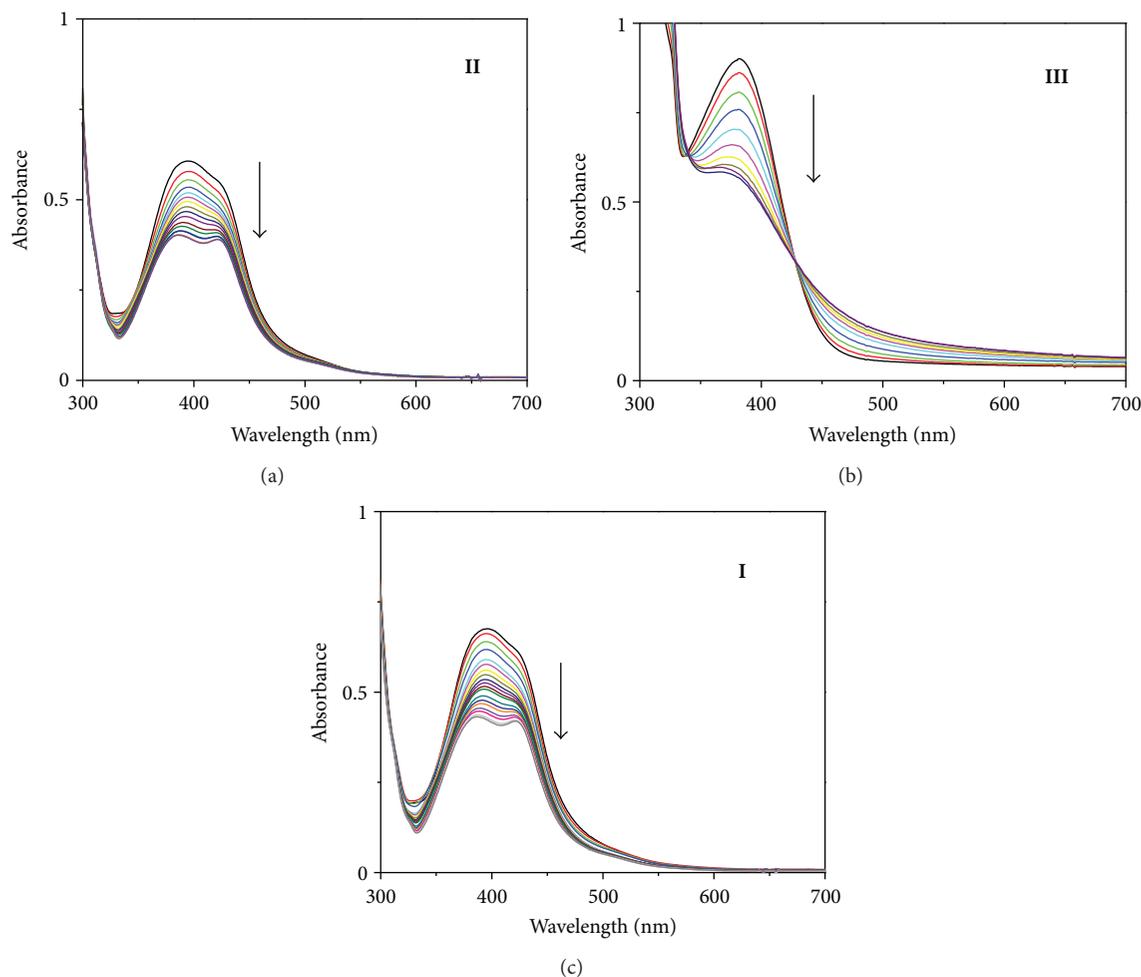


FIGURE 7: Photochemistry of complex **II** (1.5 mM in CH_3CN , $\lambda_{\text{irr}} = 420 \text{ nm}$), complex **III** (0.95 mM in CH_3CN , $\lambda_{\text{irr}} = 350 \text{ nm}$), and complex **I** (1.5 mM in CH_3CN , $\lambda_{\text{irr}} = 420 \text{ nm}$).

superposition of bands characteristics of the corresponding mononuclear complexes. The data for complex **I** show that the energy of the charge transfer band $\text{Ru}^{\text{II}} \rightarrow \text{L}$ (394 e 442 nm) remains unchanged upon the introduction of Mn ion into the Ru complex, whereas it is slightly shifted to shorter wavelength compared to the *tris*-(phenanthroline) complexes (422 and 446 nm) [9], which is characteristic of ligands serving as better π -acceptors ligands than phen.

The FTIR spectrum of **III**, shown in Figure 3, exhibit three intense $\nu(\text{CO})$ absorptions at 2041, 1953, and 1932 cm^{-1} consistent with the facial arrangement of the three COs in the coordination sphere. For complex **I**, the $\nu(\text{CO})$ stretching frequency appears as weak and broad bands around 2032 and 1940 cm^{-1} , and the two lower energy bands are overlapped suggesting the attachment of $\text{Mn}(\text{CO})_3$ unit into the Ru^{II} complex.

3.2. Electrochemistry. The voltammetric data are summarized in Table 2. Figure 4 shows a cyclic voltammogram (scan rate 100 mVs^{-1}) for a 1 mM solution of the complexes **I**, **II**, and **III** over the range 0–1.8 V (versus AG/AGCl) in acetonitrile (TBPF₆ 1 mM).

Complex **II** exhibits a redox couple at $E_{1/2} = 1.52 \text{ V}$ ($E_{\text{ox}} = 1.56 \text{ V}$ and $E_{\text{red}} = 1.49 \text{ V}$ versus Ag/AgCl) of $\text{Ru}^{\text{II/III}}$ which is more positive than those found to $[\text{Ru}(\text{phen})_3]^{2+}$ [10]. The complex **III**, on the other hand, displays a shoulder at 0.80 V corresponding to $\text{Mn}^{\text{I/II}}$ oxidation followed by an oxidation peak at 1.10 V attributed to the oxidation of Mn^{II} to Mn^{III} , which is paired with a nonreversible reductive wave at 0.90 due to $\text{Mn}^{\text{III/II}}$ reduction.

The $\text{Mn}(\text{CO})_3\text{Br}$ coordination on the $\text{Ru}(\text{phen})_2(\text{pz})_2$ did not change the redox potential values of the $\text{Ru}(\text{II})$ metal center. The cyclic voltammogram of complex **I** exhibits one irreversible oxidation at 1.10 V and two redox couple $E_{1/2}(1) = 0.76 \text{ V}$ ($E_{\text{ox}} = 0.79 \text{ V}$ and $E_{\text{red}} = 0.73 \text{ V}$ versus Ag/AgCl) and $E_{1/2}(2) = 1.52 \text{ V}$ ($E_{\text{ox}} = 1.56 \text{ V}$ and $E_{\text{red}} = 1.49 \text{ V}$ versus Ag/AgCl).

3.3. Spectroelectrochemistry. Insights into the bonding characteristics of the $\text{Ru}(\text{II})$ complexes for complexes **I** and **II** were obtained by spectroelectrochemical experiments. For the $\text{Ru}(\text{II})$ complexes, a constant potential 1.5 V (determined from cyclic voltammetry) was applied and the extent of oxidation to $\text{Ru}(\text{III})$ was monitored by UV-vis spectroscopy

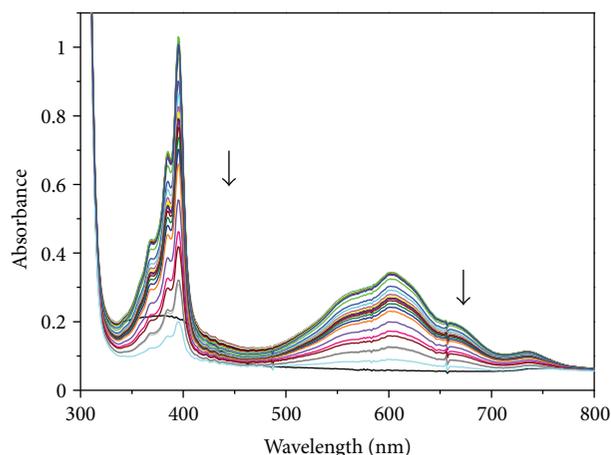
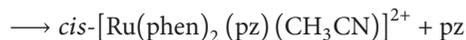


FIGURE 8: Spectral changes accompanying the consume of reduced methyl viologen ($MV^{\bullet+}$), from the thermal reaction $MV^{\bullet+} \rightarrow MV^{2+}$ in H_2O , (black line—spectrum of the mixture: complex III and MV^{2+} before irradiation).

(Figure 5). The spectrum shows the disappearance of the broad absorption band at 400 nm. After 30 min of oxidative electrolysis, the spectral changes were completed. The oxidative spectroelectrochemistry at 1.5 V leads to disappearance of the MLCT band indicating that oxidation was a $Ru^{II/III}$ process which is irreversible.

3.4. Transient Absorption Spectra. Figure 6 shows the excited state absorption spectrum for complex I in CH_3CN solution after excitation with an 8 ns pulse at 355 nm irradiation. There is a bleach of absorption band at 400 nm and new structured absorption with maxima centered at 350 nm and 600 nm consistent with formation of an MLCT ($Ru \rightarrow phen$) excited state [11].

3.5. Photochemistry. The complexes are stable in deaerated solutions in the absence of light. When solutions of complex II were subject to continuous photolysis, the resulting optical spectral changes were consistent with the substitution of only one pyrazine molecule by a solvent molecule (1) and (2)



For example, Figure 7 illustrates the spectral changes seen when an acetonitrile solution of complex I (0.22 mM) was irradiated at $\lambda_{irr} = 420$ nm, $I_0 = 1.27 \times 10^{-8}$ einstein s^{-1} . The spectra show a progressive depletion of the characteristic absorption band at 400 nm concomitant with formation of two broad shoulders at 385 and 422 nm, in accordance with the formation of complex $Ru(phen)_2(CH_3CN)_2$ [12]. For

complexes I and II, exhaustive photolysis leads to the same final stable spectrum assigned to the monosolvated complex.

3.6. Photoinduced Electron Transfer Reactions. Figure 8 shows the UV-vis spectral changes of the thermal reaction ($MV^{\bullet+} \rightarrow MV^{2+}$) of a solution containing complex III and MV^{2+} (methyl viologen) in pure water immediately after 10 s continuous irradiation at 355 nm light. Before irradiation, the absorption spectrum of the mixture shows the characteristic absorption of starting complex ($\lambda_{max} = 380$ nm). A broad absorption band with maximum near 605 nm and a peak at 394 nm appeared just after irradiation. These new absorptions match the methyl viologen radical ($MV^{\bullet+}$) absorption spectrum [13].

The photoinduced electron transfer reactions for complexes I and II did not occur, since in the UV-vis spectra was not observed any $MV^{\bullet+}$ characteristic band even after exhaustive photolysis. These results show that the intermolecular photoinduced electron transfer reaction is activated in water only in certain conditions. The presence of Ru(II) unit inhibits the MV^{2+} reduction.

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