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Synthesis and Characterization of Homoleptic and Heteroleptic Ruthenium Polypyridine Complexes

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Abstract

The homoleptic ruthenium(II) complex $\text{Ru}(\text{C}_{13}\text{H}_{10}\text{N}_2)_3(\text{PF}_6)_2$, and heteroleptic ruthenium(II) complexes $\text{Ru}(\text{C}_{13}\text{H}_{10}\text{N}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)(\text{PF}_6)_2$, and $\text{Ru}(\text{C}_{13}\text{H}_{10}\text{N}_2)(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{PF}_6)_2$ have been prepared by following the standard synthetic procedure. These complexes were then purified by repeated column chromatography. The identity and the integrity of the complexes were confirmed by elemental analysis and mass spectroscopy. The calculated and the experimental values for the elemental analysis were in good agreement. The calculated and the experimental molar masses obtained were also identical. Ultraviolet-visible absorption and emission spectroscopic methods were used to investigate the properties of these complexes. The absorption spectra of all complexes consist of a series of absorption bands in the ultraviolet and visible region. All three complexes show a strong emission band in the visible region. The emission maxima for the heteroleptic complexes are slightly red-shifted.

Introduction

There is an intense interest in designing molecular systems that will absorb visible sunlight, initiate an electron-transfer process, and ultimately convert solar energy to useful chemical energy (Kalyanasundaram 1987, Parmon and Zamarev 1989). The study of the photophysical and photochemical properties of transition-metal complexes is of great interest. Recently, most of the attention in this field has been focused on polypyridine complexes of ruthenium(II) as components of solar-energy conversion schemes (Jures et al. 1988, Kalyanasundaram 1982). These complexes offer desirable redox properties, excited-state reactivity, luminescent emission, and excited-state lifetimes. Ruthenium polypyridine complexes have been investigated for use in artificial photosynthesis and many biological electron-transfer processes. It has

been documented that ruthenium polypyridine complexes have potential use as efficient photoinitiators in electron-transfer studies (Winkler et al. 1982). This has prompted us to further investigate the properties of such complexes.

The transition-metal complex ion tris(2,2'-bipyridine)ruthenium(II) (known as $\text{Ru}(\text{bpy})_3^{2+}$, where bpy = 2,2'-bipyridine) has been intensely studied since the early 1960s. This interest arises from the suitability of this complex for systematic investigations of structural and electronic properties that influence the photophysical and photoredox processes. Numerous studies have been done on tuning the redox and excited-state properties of ruthenium(II) polypyridine complexes by the modification of ligands (Rillema et al. 1983, Ernst and Kaim 1989, Kawanishi et al. 1989, Lever 1990). A fundamental problem is determining which ligand modifications can produce a favorable excited state and redox properties and can alter inherent photophysical and photoredox properties of the parent complexes in an advantageous manner. Many electron-transfer studies require attention to this matter. This research is directed at gaining a better understanding of photophysical and photoredox properties of the homoleptic and heteroleptic targeted complexes in order to facilitate the design of electron-transfer studies.

In this paper, we report efficient synthetic methods for the preparation of $\text{Ru}(\text{Me-phen})_3(\text{PF}_6)_2$, $\text{Ru}(\text{Me-phen})_2(\text{bpy})(\text{PF}_6)_2$, and $\text{Ru}(\text{Me-phen})(\text{bpy})_2(\text{PF}_6)_2$ (where Me-phen = 5-methyl-1,10-phenanthroline and bpy = 2,2'-bipyridine) complexes (Cationic forms are shown in Figure 1). The complexes were purified by repeated column chromatography. The identity and the integrity of the complexes were confirmed by elemental analysis and mass spectroscopy. UV-vis absorption and emission spectroscopic methods were used to investigate the properties of these complexes. Spectroscopic and photophysical studies document the fact that inherently favorable photophysical properties are not substantially altered by ligand substitutions.

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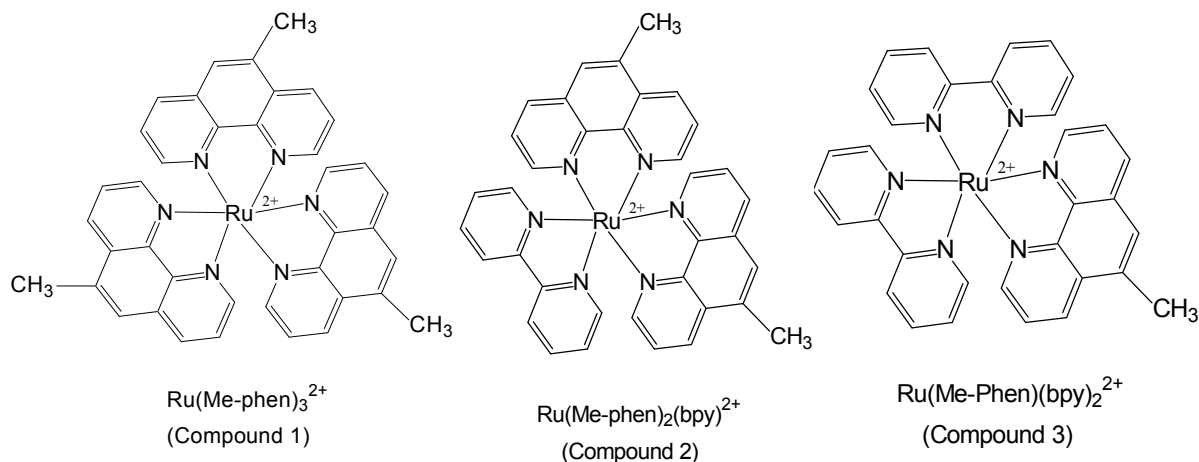


Figure 1. Schematic representation of the prepared complexes.

Materials and Methods

Chemicals

The ligand, 2,2'-bipyridine (bpy), $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, NH_4PF_6 , LiCl , and silica gel were purchased from the Aldrich Chemical Co. 5-methyl-1,10-phenanthroline (Me-phen) was purchased from Lancaster. All the chemicals were used without further purification. All solvents used were reagent grade or better.

Preparation of Compounds

Compound 1 [$\text{Ru}(\text{Me-Phen})_3(\text{PF}_6)_3$] was prepared by a modification of a method previously developed by Walker et al. (2004) by substituting 5-methyl 1,10-phenanthroline for bipyridine. The compound was prepared by the reaction of 1 mmol $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and 4 mmol Me-phen in 50 mL of ethylene glycol under an Ar atmosphere. The reaction mixture was refluxed for 4 hours. The color changed from a dark black to a bright orange in approximately an hour. The resulting solution was then cooled to room temperature and filtered. Saturated aqueous solution of ammonium hexafluorophosphate (NH_4PF_6) was added to the mixture to precipitate the tris complex as a PF_6 salt. To enhance the precipitation, the resulting mixture was left in the refrigerator overnight, and then the precipitate was collected by vacuum filtration. The precipitate was washed with plenty of water to remove excess NH_4PF_6 and finally washed with diethyl ether and dried in a desiccator. The crude tris complex was purified by silica-gel column chromatography using acetonitrile as an eluent. The first band was collected

and added dropwise to ether to reprecipitate. Typical yields of 70-80% spectroscopically pure product were obtained by this method. Elemental analysis calculated for $\text{RuC}_{39}\text{H}_{30}\text{N}_6\text{P}_2\text{F}_{12}$: C = 48.11%, H = 3.11%, N = 8.63%; experimentally found: C = 48.04%, H = 3.10%, N = 8.61%.

Compound 2 [$\text{Ru}(\text{Me-phen})_2(\text{bpy})(\text{PF}_6)_2$] was prepared by a two-step procedure. In the first step, $\text{Ru}(\text{bpy})\text{Cl}_4$ was prepared according to a previously published method (Krause 1977) by the reaction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and bpy (20% excess over one equivalent) in a 1.0 M HCl solution. The mixture was stirred at room temperature to dissolve the solids. The resulting mixture was stoppered and allowed to stand for several days, and the black product was isolated by vacuum filtration. The precipitate was washed with water and stored in a desiccator. $\text{Ru}(\text{bpy})\text{Cl}_4$ was used without further purification.

The reaction of $\text{Ru}(\text{bpy})\text{Cl}_4$ and Me-phen (1:3 molar ratio) produced compound 2. $\text{Ru}(\text{bpy})\text{Cl}_4$ (0.50 mmol) and Me-phen (1.5 mmol) were dissolved in 50 mL of an 80/20 ethanol/ H_2O mixture. The solution was refluxed for 24 hr under argon, cooled to room temperature and filtered. A saturated aqueous solution of ammonium hexafluorophosphate was added to the filtrate to precipitate the product. A brownish yellow precipitate appeared. The precipitate was collected by vacuum filtration, washed with water and diethyl ether, and stored in a desiccator. The final product was purified by column chromatography on alumina and on silica, using acetonitrile as the eluent. The first band was collected and reprecipitated by adding diethyl

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ether. The typical yield was 60-70%. Elemental analysis calculated for $\text{RuC}_{36}\text{H}_{28}\text{N}_6\text{P}_2\text{F}_{12}$: C = 46.21%, H = 3.02%, N = 8.98%; experimentally found: C = 46.52%, H = 3.10%, N = 8.78%.

Compound 3 [$\text{Ru}(\text{Me-phen})(\text{bpy})_2(\text{PF}_6)_2$] was also prepared in a two-step procedure. In the first step, $\text{cis-Ru}(\text{bpy})_2\text{Cl}_2$ was prepared from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ by a slight modification of a published method (Sullivan et al. 1978). One equivalent of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, two equivalents of bipyridine (bpy) ligand, and 0.1 equivalent of LiCl were refluxed in DMF (dimethyl formamide, 50 mL per 0.5 g of Ru salt) for approximately 6-7 hr under Ar atmosphere. The solution was constantly stirred during reflux. After reflux, the solution was cooled to room temperature and 125 mL of reagent-grade acetone was added to the reaction mixture. After stirring for a few minutes, the reaction mixture was allowed to cool overnight at -5°C in the freezer. The next morning, the resulting black precipitate (microcrystalline) was collected by vacuum filtration and washed several times with cold water. Finally, the precipitate was washed with diethyl ether and was dried under vacuum. The purity of the prepared complex was checked by thin-layer chromatography (TLC, alumina and silica plate, acetonitrile solvent) and absorption spectroscopy.

$\text{Ru}(\text{bpy})_2\text{Cl}_2$ (0.5 mmol) and Me-phen (1.0 mmol) were dissolved in 50 mL H_2O . The solution was refluxed under argon for 4 hr with stirring. The color of the solution changed from black to yellow orange during this time. The solution was cooled to room temperature and filtered. Saturated aqueous ammonium hexafluorophosphate was added to the filtrate to precipitate the product as a PF_6 salt. The precipitate was collected by vacuum filtration and washed three times with 15 mL of water followed by 50 mL of diethyl ether and dried under vacuum. The orange product was stored in a desiccator. The product was purified by column chromatography on silica using acetonitrile as an eluent. The first band was collected as the pure product and precipitated by adding diethyl ether. The typical yield was 65-75%. Elemental analysis calculated for $\text{RuC}_{33}\text{H}_{26}\text{N}_6\text{P}_2\text{F}_{12}$: C = 44.16%, H = 2.92%, N = 9.36%; experimentally found: C = 43.95%, H = 2.91%, N = 9.35%.

Results and Discussion

The synthetic method described here for compound 1 is a method used to prepare the tris-ligated metal complexes of 2,2'-bipyridine ligand (Walker et al.

2004). We substitute for the 2,2'-bipyridine ligand with 5-methyl-1,10-phenanthroline. This method is a very convenient method due to its simplicity, short reaction time, good yield, and the need for only a slight excess of ligand. The only disadvantage is the presence of trace impurities in the sample, which is confirmed by thin-layer chromatography (TLC). The product was purified by column chromatography.

The mixed-ligand complexes compound 2 and compound 3 involve two-step procedures. The precursor complexes $\text{Ru}(\text{bpy})\text{Cl}_4$ and $\text{Ru}(\text{bpy})_2\text{Cl}_2$ were prepared according to published methods (Krause 1977, Sullivan et al. 1978) and used without further purification. The targeted complexes were prepared by the reaction of precursor complexes and additional ligands. This type of procedure is a standard and common procedure for mixed-ligand complexes (Bhuiyan et al. 2008, Bhuiyan 2008, Bhuiyan and Kincaid 1999). Thin-layer chromatography indicates that all three compounds were slightly contaminated. We used the most common purification method of column chromatography on silica using acetonitrile as an eluent for all three complexes. We were able to remove all the impurities from compound 1 and compound 3, but compound 2 still contained one impurity. Mass spectroscopy indicated that compound 2 was contaminated by a trace amount of compound 1. Most likely, during the reaction, a small amount of bpy ligand was substituted by phenanthroline ligand and a trace amount of compound 1 was formed. Finally, we were able to remove this impurity by using an alumina column followed by a silica column using acetonitrile as an eluent.

The identity and the integrity of the complexes were confirmed by elemental analysis (Columbia Analytical Services) and mass spectroscopy (Arkansas State Wide Mass Spectrometry Facility). The results of experimental elemental analysis are in good agreement with the calculated results (shown in the Materials and Methods section). Electrospray mass spectral measurements were performed with a Bruker Esquire LCMS at the University of Arkansas, Fayetteville. All the samples were dissolved in acetonitrile and were injected directly with a flow rate of approximately $50 \mu\text{L min}^{-1}$ with nitrogen nebulizing gas. The mass spectra are shown in Figure 2. Trace A is for compound 1, trace B is for compound 2, and trace C is for compound 3. The calculated molar masses for the complexes are 683.8 [$\text{Ru}(\text{Me-phen})_3^{2+}$], 645.7 [$\text{Ru}(\text{Me-phen})_2(\text{bpy})^{2+}$], and 607.7 [$\text{Ru}(\text{Me-phen})(\text{bpy})_2^{2+}$], respectively. The electrospray mass spectrometry of the complexes showed a consistent fragmentation

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pattern (shown in Figure 2). Each spectrum showed the molecular-ion peak as the most abundant peak. The molecular-ion peaks appear at m/z (mass/charge) = 341.9 (trace A), m/z = 322.9 (trace B), and m/z = 303.9 (trace C). From isotopic patterns, it was confirmed that each ion has an overall charge of 2+, so the experimental molar masses are 683.8 (trace A), 645.8 (trace B), and 607.8 (trace C) for compound 1, compound 2 and compound 3, respectively. The experimental molar masses are in very good agreement with the calculated molar masses, which confirms the identity and the integrity of the compounds.

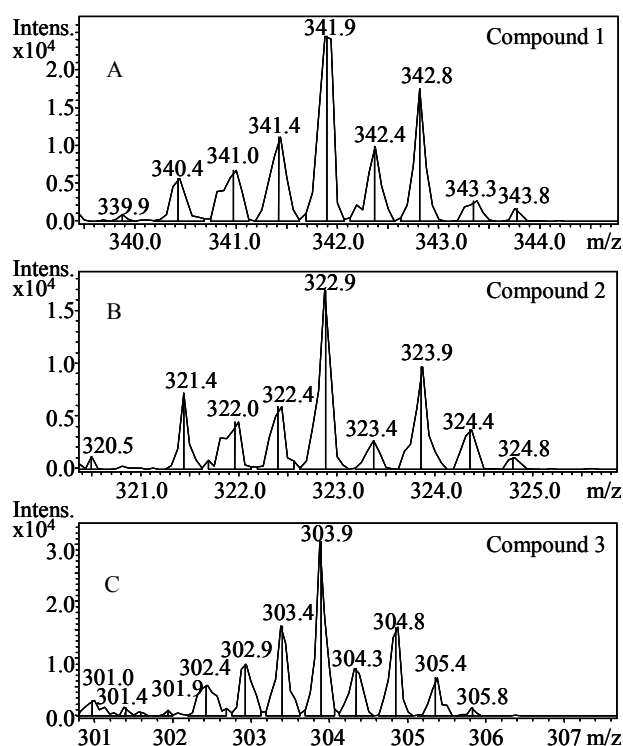


Figure 2. The electrospray mass spectra of the prepared complexes, showing the major fragment cluster.

Electronic absorption spectra were obtained with a Shimadzu model UV-2501 PC UV-vis recording spectrophotometer using a 1-cm quartz cuvette. Spectra were obtained in the absorbance mode. The electronic absorption spectra of all the complexes were measured in acetonitrile solution and are shown in Figure 3. The solid-line spectrum is for compound 1 (trace A), the dotted line is for compound 2 (trace B), and the dashed line is for compound 3 (trace C). The absorption spectra of the complexes consist of a series of

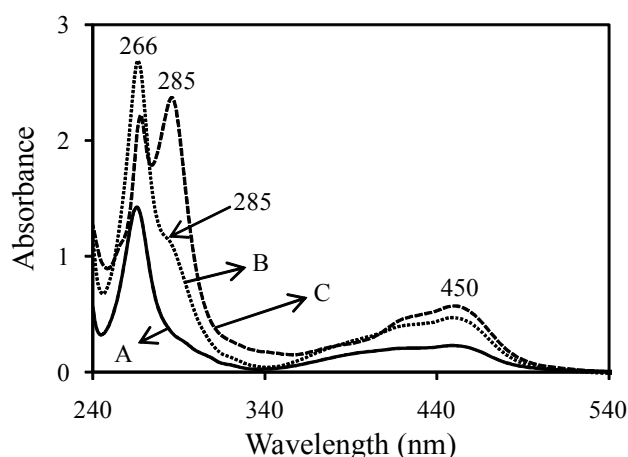


Figure 3. Electronic absorption spectra of the prepared complexes: Compound 1 (trace A); Compound 2 (trace B); and Compound 3 (trace C).

absorption bands in the UV and visible region. A very strong transition at 266 nm is assigned to a spin-allowed ligand-centered $\pi-\pi^*$ transition of Me-phen ligand, and a 285 nm is assigned to a $\pi-\pi^*$ transition of bpy ligand (Kalyanasundaram and Nazeeruddin 1990). This is confirmed by comparison with the absorption spectra of the free Me-phen and bpy ligands. Compound 1 does not contain any bpy ligand, and the 285 nm absorption band is totally absent in the absorption spectrum (trace A). Compound 2 contains a 285 nm band as a weak shoulder because of one bpy ligand (trace B), and compound 3 contains a strong band at 285 nm because of two bpy ligands (trace C). The broad, relatively intense visible band at 450 nm is assigned to a metal-to-ligand charge transfer (MLCT) transition by comparing with other ruthenium(II) polypyridine complexes (Denti et al. 1990). The higher-energy shoulder observed is assigned to a second MLCT transition.

The electronic emission spectra were obtained with a PerkinElmer Model LS 55 luminescence spectrometer with 450 nm excitation. All the emission spectra of the complexes were measured in acetonitrile solution at room temperature. Excitation wavelength was decided by scanning the excitation spectra at a fixed emission wavelength. The excitation wavelength was determined to be 450 nm for all three complexes. The emission spectra of all the complexes are shown in Figure 4. The solid line is for compound 1 (trace A), the dotted line is for compound 2 (trace B), and the dashed line is for compound 3 (trace C). The electronic emission spectra of the complexes exhibit strong

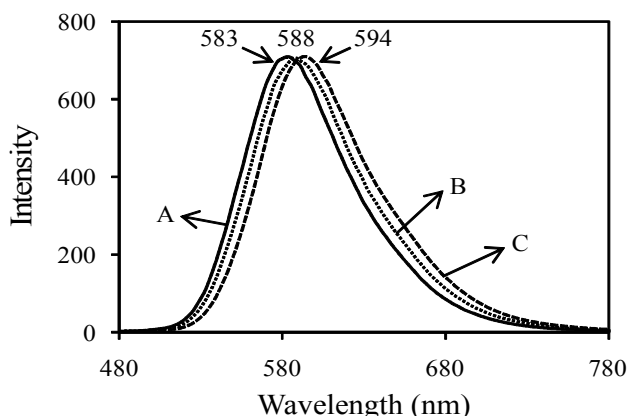


Figure 4. Electronic emission spectra of the prepared complexes: Compound 1 (trace A); Compound 2 (trace B); and Compound 3 (trace C).

emission bands at 583 nm (compound 1), at 588 nm (compound 2), and at 594 nm (compound 3), respectively. All three complexes exhibit a single emission band, which confirms the purity of the prepared complexes. As for other polypyridine complexes of Ru(II), these luminescence bands have been assigned as phosphorescent process $^3\text{MLCT}$ (triplet metal-to-ligand charge transfer) \rightarrow ^1GS (singlet ground state) (Lytle and Hercules 1969, Bhuiyan and Kincaid 2001), the $^3\text{MLCT}$ state being reached by rapid intersystem crossing from the lowest $^1\text{MLCT}$ state. The emission band for compound 2 is slightly red shifted from that observed for compound 1 (588 nm vs. 583 nm) because of one bpy ligand. The spectrum of compound 3 is 6 nm red shifted (two bpy ligands) with respect to that of compound 2 (one bpy ligand). This observation is consistent with the previously reported spectra of similar ruthenium(II) polypyridine complexes.

Conclusions

The present studies summarize efficient synthetic methods for the preparation of homoleptic and heteroleptic ruthenium(II) polypyridine complexes. Elemental analysis and spectroscopic and photophysical studies confirm the identity and structural integrity of the prepared complexes. It was observed that the inherently favorable photophysical properties are not substantially altered by the ligand substitution. These complexes may be viewed as attractive precursors for the construction of high-charge mononuclear complexes by the modification of the attached methyl group of the phenanthroline ligand.

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