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Synthesis, Characterization, and Properties of Mononuclear and Dinuclear Ruthenium(II) Complexes Containing Phenanthroline and Chlorophenanthroline

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Running Title: Mononuclear and Dinuclear Ruthenium(II) Complexes with Phenanthroline and Chlorophenanthroline

Abstract

The study of photophysical and photochemical properties of ruthenium complexes is of great interest for fundamental practical reasons. Ruthenium complexes have been investigated for use in artificial photosynthesis. This paper deals with the synthesis and spectroscopic investigation of custom-designed ruthenium complexes containing phenanthroline and chloro-phenanthroline ligands. These complexes may be useful for biological electron-transfer studies. The heteroleptic ruthenium monomer complex $\text{Ru}(\text{phen})_2(\text{Cl-phen})$ (where phen = 1,10-phenanthroline and Cl-phen = 5-chloro-1,10-phenanthroline) was prepared in a two-step procedure previously developed in our laboratory. This monomer complex was used to prepare the ruthenium homometallic dimer complex, $(\text{phen})_2\text{Ru}(\text{phen-phen})\text{Ru}(\text{phen})_2$, by utilizing the Ni-catalyzed coupling reaction. Both complexes were purified by extensive column chromatography. The identity and the integrity of the monomer complex were confirmed by elemental analysis. The calculated and the experimental values for the elemental analysis were in good agreement for the monomer complex. UV/Vis absorption spectroscopy, emission spectroscopy, and cyclic voltammetry were used to investigate the properties of both the complexes.

Introduction

Photosynthesis is a vital process that produces glucose and oxygen from carbon dioxide and water in the presence of chlorophyll by using solar energy (Lawlor 1993). Solar light at the Earth's surface is mostly visible and infra-red light with a small fraction of ultraviolet light. In photosynthesis, green plants harness solar energy and convert it to chemical energy by splitting water. For the past 25 years, there has been interest in designing chemical processes that can work

like photosynthesis. Molecular hydrogen can reduce our dependence on fossil fuels, which can reduce the emission of greenhouse gases. Hydrogen is a very logical choice as a fuel for the future, production cost currently renders its production and use as unfeasible. Solar radiation is a virtually inexhaustible source of energy that can be converted to environmentally clean fuels once a molecular suprastructure that will mimic photosynthesis can be developed. Currently, transition-metal complexes are being investigated as potential photosensitizers.

There are several challenges in the photocatalytic synthetic system to produce hydrogen by the reduction of water. The issues of concern are (1) a suitable photosensitizer from the view point of absorption of sunlight, (2) production of a reasonably long lasting excited-state, (3) reduction of wasteful reverse electron transfer process, (4) favorable ground and excited state potential of the redox species, and (5) regeneration of the photochemical cycle. Experiments have been attempted to find the solution to the challenges mentioned above, and the most innovative solutions are made by using ruthenium polypyridine complexes (Kalyanasundaram 1982 and 1987, Ramamurthy 1991, Downard et al. 1991). In this paper, we report two new complexes that offer desirable redox potential and suitable photophysical properties as photocatalysts.

Many important biological processes such as photosynthesis, mitochondrial respiration, and intermediary metabolism involve electron-transfer reactions. Photoactive ruthenium complexes were used to understand the mechanism of biological electron-transfer processes (Zaslavsky et al. 1998). It was found that the overall charge on the complex plays a critical role in protein binding and photoreduction or photooxidation efficiency. Ruthenium complexes with higher charge bind more tightly with the protein by electrostatic interaction. Dinuclear ruthenium complexes with an overall charge of +4 are capable of

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photoreducing protein with a 5-fold greater yield than mononuclear complexes (Sadoski et al. 2000). This study prompted us to synthesize custom-designed dinuclear complexes.

There is only one published procedure for the synthesis of the free bridging ligand phen-phen (5,5-bis(1,10-phenanthroline)) by a metal-catalyzed coupling reaction (Toyota et al. 2005). The yield was extremely low, and the product was very contaminated. It was very difficult and time consuming to purify the bridging ligand. Griffiths and coworkers (2000) attempted to apply a nickel coupling reaction to 5-chloro-1,10-phenanthroline (Cl-phen) to form free ligand, but it was not successful because of destabilization of the nickel catalyst. However, they were successful in coupling the ruthenium, osmium, and iridium mixed-ligand complexes with very good yield.

In our previous publication (Bhuiyan and Kudo 2011), we reported the efficient synthetic method for the preparation of the heteroleptic ruthenium monomer complex $\text{Ru}(\text{Cl-phen})(\text{bpy})_2(\text{PF}_6)_2$ and the ruthenium dimer complex $(\text{bpy})_2\text{Ru}(\text{phen-phen})\text{Ru}(\text{bpy})_2$ (where bpy = 2,2'-bipyridine and Cl-phen = 5-methyl-1,10-phenanthroline). In this paper, we are reporting the synthesis and characterization of two new complexes. Heteroleptic ruthenium monomer complex $\text{Ru}(\text{phen})_2(\text{Cl-phen})$ (where phen = 1,10-phenanthroline and Cl-phen = 5-chloro-1,10-phenanthroline) was prepared in a two-step procedure previously developed in our laboratory. This monomer complex was used to prepare the ruthenium homometallic dimer complex, $(\text{phen})_2\text{Ru}(\text{phen-phen})\text{Ru}(\text{phen})_2$, by utilizing the Ni-catalyzed coupling reaction. Both complexes were purified by extensive column chromatography. The identity and the integrity of the monomer complex were confirmed by elemental analysis. UV/Vis absorption spectroscopy, emission spectroscopy, and cyclic voltammetry were used to investigate the properties of both the complexes.

Materials and Methods

Chemicals

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, 1,10-phenanthroline, LiCl, dimethylformamide (DMF), acetone, diethyl ether, 5-chloro-1,10-phenanthroline, NH_4PF_6 , alumina, high-purity silica gel, nickel (II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), triphenylphosphine (PPh_3), zinc dust, and tetraethyl ammonium iodide (Et_4NI) were purchased from the Aldrich Chemical Company. All

the chemicals were used as purchased without further purification. All solvents used were reagent grade or better.

Measurements

Elemental analysis was performed by Columbia Analytical Services, Tucson, AZ. 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 solutions. The electronic emission spectra were obtained with a PerkinElmer Model LS 55 luminescence instrument. The emission spectra of the monomer and the dimer complexes were measured in acetonitrile solutions at room temperature. Cyclic voltammetry was performed with an Epsilon BASi Instruments Electrochemical Analyzer. The working electrode was a 2-mm-diameter carbon-disk, the auxiliary electrode was platinum wire and the reference electrode was a saturated calomel electrode from BASi Instruments. Cyclic voltammograms were recorded in 0.1M $(\text{Bu}_4\text{N})(\text{PF}_6)$ (tetrabutylammonium hexafluorophosphate) in CH_3CN .

Preparation of Compounds

The monomer complex, $\text{Ru}(\text{phen})_2(\text{Cl-phen})(\text{PF}_6)_2$, was prepared in a two-step process by a method previously developed in our laboratory for bipyridine ligand (Bhuiyan et al. 2010). The first step was to prepare the precursor complex for the monomer. The synthetic procedure is shown in Scheme 1.

The second step to prepare the monomer from the precursor complex is shown in Scheme 2.

The product was vacuum dried and placed in a desiccator. The product was purified on an alumina column and silica-gel column with CH_3CN as an eluent. The first band was collected and added dropwise to diethyl ether to precipitate the product. The typical yield was about 55%. Elemental analysis calculated for $\text{RuC}_{36}\text{H}_{23}\text{N}_6\text{ClPF}_6$: C = 44.78%, H = 2.40%, N = 8.70%; experimentally found: C = 43.25%, H = 2.56%, N = 8.67%

The dimer complex, $(\text{phen})_2\text{Ru}(\text{phen-phen})\text{Ru}(\text{phen})_2^{4+}$, was prepared from the monomer complex, $\text{Ru}(\text{phen})_2(\text{Cl-phen})(\text{PF}_6)_2$, by the Ni-catalyzed direct coupling reaction (Bhuiyan and Kudo 2011). The synthetic procedure is shown in Scheme 3.

Scheme 1. Synthesis of $\text{Ru}(\text{phen})_2\text{Cl}_2$ precursor complex Scheme 2. Synthesis of $\text{Ru}(\text{phen})_2(\text{Cl-phen})^{2+}$ monomer complex

The ruthenium dimer product was precipitated as a PF_6 salt by adding aqueous ammonium NH_4PF_6 . The precipitate was collected by vacuum filtration. The precipitate was washed with cold water to remove excess NH_4PF_6 , and was finally washed with diethyl ether. After the precipitate was dried in a desiccator,

Scheme 3. Synthetic scheme of ruthenium dimer complex

the crude compound was purified by column chromatography using silica-gel and alumina stationary phases and acetonitrile as an eluent. The first band was collected and added dropwise to diethyl ether to precipitate the product. Typically a 55% yield was obtained.

Results and Discussion

The monomer complex, $\text{Ru}(\text{phen})_2(\text{Cl-phen})(\text{PF}_6)_2$, was prepared in a two-step process by a method previously developed in our laboratory for bipyridine ligand (Bhuiyan et al. 2010). In the first step, the precursor complex $\text{Ru}(\text{phen})_2\text{Cl}_2$ was prepared following the similar procedure of $\text{Ru}(\text{bpy})_2\text{Cl}_2$. The second step involved the reaction of the previously prepared precursor complex and additional Cl-phen ligand. This type of procedure is common for mixed-ligand complexes (Bhuiyan 2008, Bhuiyan et al. 2008, Bhuiyan and Kincaid 1999, Bhuiyan et al. 2009). We used the most common purification method of column chromatography on alumina and silica with acetonitrile as an eluent for the complex (Bhuiyan et al. 2010, Bhuiyan and Kudo 2011).

The homometallic dinuclear ruthenium dimer complex, $(\text{phen})_2\text{Ru}(\text{phen-phen})\text{Ru}(\text{phen})_2^{4+}$, was formed by the nickel-catalyzed direct coupling of the

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monomer complex by following the procedure mentioned in the literature for free ligands as well as other metal complexes (Griffiths et al. 2000, Johansson et al. 2000, Toyota et al. 2005). The requirement to maintain an inert atmosphere during the synthesis is very critical. This nickel-catalyzed coupling reaction is very sensitive to traces of oxygen. Also, a stable temperature plays a significant role in the synthesis. The temperature needs to be between 55 °C to 57 °C for the whole reaction time to obtain satisfactory product. The color changes during the reaction are obvious and are a good indication of a satisfactory reaction. The color turned from blue to green, then yellow, then orange and finally reddish brown within the first 30 minutes.

Electronic absorption spectra of the monomer and dimer complexes are shown in Figure 1. The solid-line spectrum is for the dimer complex (trace A) and the dashed line is for the monomer complex (trace B). The absorption spectrum of the dimer complex is very similar to that of the monomer complex. Both spectra consist of absorption bands in the UV and visible regions. The very intense UV band is assigned to a spin-allowed ligand-centered π to π^* transition of the phen ligand (Kalyanasundaram and Nazeeruddin 1990). The broad, relatively intense visible band at ~450 nm is assigned to a d to π^* metal-to-ligand charge-transfer (MLCT) transition, based upon data from other ruthenium(II) polypyridine complexes (Denti et al. 1990). The higher-energy shoulder observed is assigned to a second MLCT transition. It was observed that dimer formation did not affect the absorption pattern. These absorption spectra match those we previously reported for similar monomer and dimer complexes (Bhuiyan and Kudo 2011).

Figure 1. Absorption spectra of the prepared complexes in acetonitrile: dimer (trace A) and monomer (trace B).

The room-temperature emission spectra of the monomer and dimer complexes are shown in Figure 2. The excitation wavelength is 450 nm for both the complexes. The solid line is for the dimer complex (trace A) and the dashed line is for the monomer complex (trace B). The electronic emission spectra of the complexes exhibit strong emission bands at 605 nm for the dimer and at 610 nm for the monomer. Both complexes exhibit a single emission band, which confirms the purity of the prepared complexes.

Figure 2. Electronic emission spectra of the prepared complexes in acetonitrile : dimer (trace A) and monomer (trace B).

The dimer complex is 5 nm blue-shifted from the monomer complex (605 nm vs. 610 nm), which is consistent with our previous study of similar complexes (608 nm vs. 613 nm) (Bhuiyan and Kudo 2011). This observation is also consistent with the literature reports for similar types of complexes (Griffiths et al. 2000, Johansson et al. 2000). By comparing with other polypyridine complexes of Ru(II), these emission bands have been assigned to a $^3\text{MLCT}$ (triplet metal-to-ligand charge transfer) to ^1GS (singlet ground state) transition (Lytle and Hercules 1969, Bhuiyan and Kincaid 2001).

Cyclic voltammograms of the prepared monomer and dimer complexes are shown in Figure 3. The solid line is for the dimer complex and the dashed line is for the monomer complex. Both the complexes exhibit a single reversible electrochemical wave over the range examined. For each of the complexes, the potential corresponds to oxidation of ruthenium(II) to ruthenium(III). The potentials are $E_{1/2} = +1.27$ V for the monomer complex and $E_{1/2} = +1.29$ V for the dimer complex. The single wave for each complex confirms the purity of the prepared complexes. The formation of dimer shifts the wave to slightly higher potential. This

phenomenon indicates that the dimer formation did not change the energy levels significantly (Rillema et al. 1987).

Figure 3. Cyclic voltammograms of the prepared complexes: solid line is for the dimer and the dashed line is for the monomer.

Conclusions

The present report describes the efficient synthetic methods for the preparation of the mononuclear ruthenium complex, $\text{Ru}(\text{phen})_2(\text{Cl-phen})^{2+}$, and a homometallic dinuclear ruthenium complex, $(\text{phen})_2\text{Ru}(\text{phen-phen})\text{Ru}(\text{phen})_2^{4+}$. The monomer complex was prepared in a two-step process. The dimer complex is formed by the nickel-catalyzed direct coupling of the monomer complex with a very good yield (55%). Elemental analysis confirms the identity and integrity of the prepared monomer complex. Absorption, emission, and cyclic voltammetric results of the dimer complex were very comparable with those for the monomer complex and were comparable with the reported results for similar ruthenium compounds. It was observed that the inherently favorable photophysical properties are not substantially altered by dimer formation. This high-charge dimer complex can be used for metallo-protein electron-transfer studies.

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