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Laboratories and Demonstrations

Ligand Substituent Effects on Ruthenium(III/II) Redox Properties: An Advanced Inorganic Laboratory Experiment

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One advantage of using β-diketonate ligands is the large variety of substituents they offer.

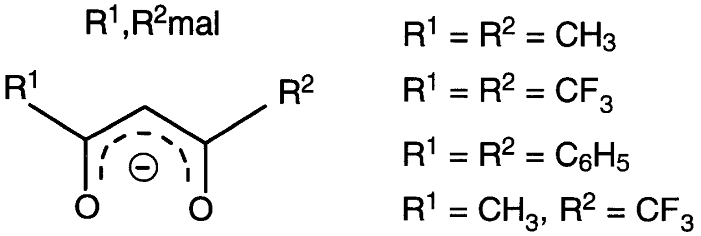
A convenient inorganic laboratory exercise is presented that exposes the student to the influences of ligand substituents on a metal center's redox properties. Students prepare a series of compounds with the general formula $[Ru(bpy)_2(R^1,R^2mal)](PF_6)$, where bpy is 2,2'-bipyridine and R^1,R^2mal is an anionic *β*-diketone ligand with various R^1 and R^2 substituents. Each complex is prepared in a single synthetic step, and the Ru(III)/Ru(II) couple is characterized by cyclic voltammetry. The potential of the Ru(III)/Ru(II) couple shifts upon varying R^1 and R^2 from 0.64 to 1.10 volts vs. SSCE in the following order: $(R^1 = R^2 = Me) < (R^1 = R^2 = Ph) < (R^1 = Me, R^2 = CF_3) < (R^1 = R^2 = CF_3)$. The inductive effects of the R substituents on the Ru(III)/Ru(II) couple are consistent with their electron-donating and electron-withdrawing properties. Hammett constants for the substituents provide an approximate measure of these effects. A linear relationship is observed when the Hammett constants are plotted against the

Ru(III)/Ru(II) potential. This laboratory exercise applies a versatile electroanalytical method, cyclic voltammetry, to measure the substituent effects on a metal center's electron density. Student results of the syntheses and redox characterizations of a series of $[Ru(bpy)_2(R^1,R^2mal)]^+$ complexes are presented and discussed.

Introduction

Over the last twenty years, many investigations have involved ruthenium(II) complexes as redox catalysts [1–5] and as model systems for the study of electron-transfer reactions [6–11]. Ruthenium compounds were chosen in these studies primarily due to the extensive methodology that has been developed for their syntheses. Many of these studies have involved bidentate ligands, such as 2,2'-bipyridine (bpy), due to their ability to form stable chelates. For example, the precursor complex $Ru(bpy)_2Cl_2$ has been used to prepare a large variety of $[Ru(bpy)_2L_2]^{n+}$ complexes in order to investigate the ability to regulate the photophysical, photochemical, and redox properties, by way of the ligand, L, and its substituents [12, 13]. The coordinated chlorides on $Ru(bpy)_2Cl_2$ are substitutionally labile under appropriate solvent conditions, which allows a broad range of $[Ru(bpy)_2L_2]^{n+}$ compounds to be conveniently prepared and studied.

The *β*-diketonates (R^1,R^2mal) are a well-known family of anionic bidentate ligands that form stable chelates with a wide variety of metal ions [14].



One advantage of using *β*-diketonate ligands is the large variety of substituents they offer. Redox potentials of a number of $[Ru(bpy)_n(R^1,R^2mal)_{3-n}]^{(n-1)+}$ complexes have been measured; these depend significantly upon the substituents of the β-diketonate ligands [15, 16]. The pseudo-octahedral $[Ru(bpy)_2(R^1,R^2mal)]^+$ systems exhibit well-behaved reversible Ru(III)/Ru(II) couples well within the solvent windows of commonly used organic solvents. The ruthenium's coordination sites are

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substitutionally inert primarily due to the chelating properties of the bipyridine and β-diketonate ligands, and the low-spin d^5 and d^6 configurations of the metal center.

Metal β-diketonate complexes have traditionally been used in physical or inorganic lab texts for investigating magnetic susceptibility properties; however, laboratory exercises involving redox manipulation by way of ligand substituents have not emerged. Preparation of the $[Ru(bpy)_2(R^1,R^2mal)]^+$ complexes is a relatively simple one-step reaction, and the precursor complex, $Ru(bpy)_2Cl_2$, and the β-diketones with various R^1 and R^2 substituents are commercially available. The synthesis and Ru(III)/Ru(II) redox characterization of these complexes has proven to be an ideal advanced inorganic laboratory exercise for students to investigate the ability to tune the redox potential by simply changing the inductive properties of the ligand substituents. In addition, this exercise exposes the student to a common and inexpensive electroanalytical technique, cyclic voltammetry, which is a direct and simple method of measuring the half-wave potential ($E_{1/2}$) of electroactive systems.

Experimental

Materials

Reagent grade solvents and chemicals were used in the synthesis of the ruthenium complexes. The β-diketones, NH_4PF_6, and $Ru(bpy)_2Cl_2$ were purchased from Aldrich. Tetrabutylammonium hexafluorophosphate (TBAH) is also commercially available (Bioanalytical Systems), or it can be conveniently synthesized [17].

Measurements

Electrochemical measurements of the ruthenium complexes were obtained using a Princeton Applied Research Model 250 Versastat/Potentiostat. Both EG&G and Bioanalytical Systems have electrochemical equipment that is more than adequate to perform cyclic voltammetry as well as many other electroanalytical techniques. Both companies offer student-friendly software to operate their equipment. Prices generally range from $7,000 to $30,000, depending upon the model and its versatility. Working and auxiliary electrodes were platinum disk electrodes (Bioanalytical Systems). Measurements were conducted in 0.1 molar solutions of TBAH in HPLC-grade acetonitrile stored over 4-*Å* molecular sieves to minimize the water content. Potentials were measured vs. a saturated sodium calomel electrode (SSCE). The SSCE electrode is a slight modification of the SCE electrode (Fisher) in which a saturated solution of

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NaCl (instead of KCl) is used to fill the electrode. The half-wave potential was calculated using the equation $E_{1/2} = (E_{p,a} + E_{p,c})/2$, where $E_{p,a}$ and $E_{p,c}$ are the peak anodic and peak cathodic potentials, respectively. The redox measurements required only several milligrams of the compound of interest dissolved in approximately 1 mL of solution in a 25–30-mL glass cell with the working, auxiliary, and reference electrodes. The cyclic voltammograms were measured at room temperature with a scan rate of 100 millivolts per second, from an initial 0.0 volts to 1.1 volts, a reversed scan to –0.2 volts, and then the potential was returned to its initial value.

In some cases, the voltammograms of the compounds exhibited irreversible oxidation at approximately 1.0 volts vs. SSCE. This was determined to be the oxidation of chlorides from two sources: the reference electrode leaking too quickly, or a ruthenium compound that was not washed well enough with water, resulting in residual chloride salts in the sample.

Synthesis of $[Ru(bpy)_2(R^1,R^2mal)](PF_6)$

$Ru(bpy)Cl_2$ (100 mg, 0.206 mmol) and 7 mole equivalents of the appropriate *β*-diketone (1.4 mmol) were added to 40 mL of 50% ethanol–H_2O and heated at reflux under nitrogen for 2 to 3 hours (Note: the *β*-diketone where R^1 and R^2 are phenyl groups required 70–80% ethanol to increase its solubility). The reaction mixture was allowed to cool to room temperature (Note: to decrease its solubility, the complex with the phenyl substituents had its volume reduced by nearly one-half using a rotary evaporator). Next, a large excess of ammonium hexafluorophosphate (300 mg, 1.84 mmol) in 100 mL of H_2O was added to the reaction mixture; this resulted in the immediate precipitation of the desired product. The solid was isolated by suction filtration, washed with H_2O (10 mL), and washed with anhydrous diethyl ether (20 mL). The product was placed under vacuum to further dry. The yields were 50–80%. Further purification can be accomplished on a neutral alumina column with acetonitrile–toluene as eluent; however, the crude product is typically pure enough to obtain very good redox data from cyclic voltammetry.

Safety Precautions

All the *β*-diketones, except for dibenzoylmethane, are flammable liquids. The trifluoro- and hexafluoro-*β*-diketones are considered irritants, and should be handled with gloves under a hood. Discarded solutions of these compounds need to be

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disposed of as halogenated waste. Both $Ru(bpy)_2Cl_2$ and acetylacetone are toxic and should be handled with gloves. It is a good rule of thumb to treat all ruthenium compounds as toxic materials; they should be disposed of accordingly.

Results

The $[Ru(bpy)_2(R^1,R^2mal)]^+$ complexes investigated exhibit reversible, one-electron Ru(III)/Ru(II) couples over the range of 0.64 to 1.10 V versus SSCE in 0.1 M TBAH in acetonitrile. The substituent effects on the $[Ru(bpy)_2(R^1,R^2mal)]^{+2/+1}$ couple are in the anodic direction and vary with R^1 and R^2 in the following order (see Table 1): ($R^1 = R^2 = CH_3$) < ($R^1 = R^2 = C_6H_5$) < ($R^1 = CH_3$, $R^2 = CF_3$) < ($R^1 = R^2 = CF_3$). The shifts in the Ru(III)/Ru(II) redox couples are consistent with the electron-donating and electron-withdrawing nature of the substituents on the β-diketonate ligands.

The metal diketonate forms a six-membered ring in which the substituents, R^1 and R^2, are in the meta position relative to the ruthenium center. Hammett constants provide an approximate measure of inductive effects from substituents in *meta* or *para* positions relative to the site of interest [18].

A plot of $E_{1/2}$ for the $[Ru(bpy)_2(R^1,R^2mal)]^{+2/+1}$ couple vs. the sum of the Hammett constants for the β-diketonate substituents is shown in Figure 1. The linear relationship reflects how the electron density on the metal center corresponds to the electron-withdrawing and electron-donating abilities of the substituents.

For example, when the CH_3 groups are replaced with the more electron-withdrawing CF_3 groups, the electron density on the metal center is reduced considerably; this results in a higher redox potential. Other studies have also reported linear relationships between Ru(III)/Ru(II) redox potentials and substituent Hammett constants in ruthenium complexes containing β-diketonate ligands [16, 19–21].

Conclusions

The synthesis of a series of compounds with the general formula $[Ru(bpy)_2(R^1,R^2mal)](PF_6)$ is relatively straightforward. These complexes provide a convenient advanced inorganic laboratory exercise that allows students to investigate ligand substitution and how the electron density on a metal center can be influenced by the electron-donating and electron-withdrawing natures of ligand substituents. The

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TABLE 1. Cyclic Voltammetry Data For $[Ru(bpy)_2(R^1,R^2mal)]^{+2/+1}$ Redox Couple and Sum of Hammett Constants for the β-diketonate Substituents.

Complex	$E_{1/2}(V)^a$	$\Sigma(\sigma_m)$
$[Ru(bpy)_2((CF_3)_2mal)]^{+2/+1}$	1.10	0.86
$[Ru(bpy)_2(CH_3CF_3\ mal)]^{+2/+1}$	0.86	0.36
$[Ru(bpy)_2((C_6H_5)_2mal)]^{+2/+1}$	0.68	0.12
$[Ru(bpy)_2((CH_3)_2mal)]^{+2/+1}$	0.64	-0.14

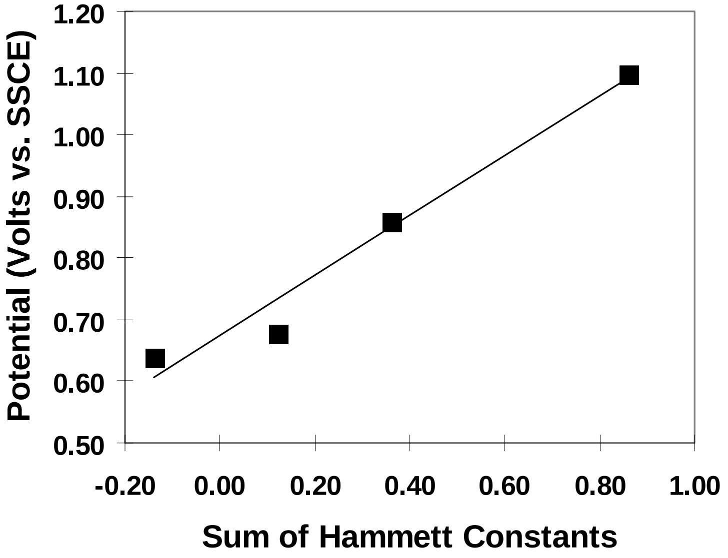

FIGURE 1. PLOT OF REDOX POTENTIAL ($E_{1/2}$) VS. THE SUM OF HAMMETT CONSTANTS.

inductive effects allow one to tune the Ru(III)/Ru(II) redox potential in a rational manner by selecting the appropriate substituents. Further fine tuning can be explored with other existing variations of the substituents on the β-diketonate ligand [19, 21]. In addition, students are exposed to one of the most versatile electroanalytical techniques, cyclic voltammetry, for investigating and comparing the redox properties of

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electroactive organic and inorganic systems. There are several excellent overviews of cyclic voltammetry [22–25].

With this series of compounds the students can also explore the effects that the β-diketonate substituents have on the electronic spectroscopy. For example, the visible range is dominated by metal-to-ligand charge-transfer bands in which the lowest energy bands are metal d$\pi \rightarrow \pi^*$ (bpy) transitions. The substituents influence the energy of the metal's filled dπ orbitals, as evidenced by the shift in the Ru(III)/Ru(II) redox potential. In contrast, the substituents are not expected to greatly affect the energy of the empty π^* (bpy) orbitals. Therefore, a shift in the absorbance energy should correlate with a change in the metal's redox potential. However, it is important to consider the low symmetry of these compounds because it removes the degeneracy of the metal dπ and ligand π^* orbitals making the absorbance spectra difficult to interpret.

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