1993

Synthesis and Characterization of Transition Metal Polypyridyl Complexes with a Novel 1,10-Phenanthropteridinedione Ligand

Huakai Huang

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Synthesis and Characterization of Transition Metal Polypyridyl Complexes with a Novel 1,10-Phenanthropteridinedione Ligand

BY

Huakai Huang

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Master of Science in Chemistry

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1993

I HEREBY RECOMMEND THIS THESIS BE ACCEPTED ASFULFILLING THIS PART OF THE GRADUATE DEGREE CITED ABOVE

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Synthesis and Characterization of Transition Metal Polypyridyl Complexes with a Novel 1,10-Phenanthropteridinedione Ligand
Title of Thesis: Synthesis and Characterization of Transition Metal Polypyridyl Complexes with a Novel 1,10-Phenanthropteridinedione Ligand

Name: Huakai Huang
Thesis directed by: Dr. Mark E. McGuire

A new alloxazine ligand (1; "Pptd"), produced by the condensation of 1,10-phenanthroline-5,6-dione with 5,6-diamino-1,3-dimethyluracil, and several transition metal complexes containing this ligand, have been synthesized. The Pptd ligands attach to Ru(II), Co(II), or Re(I) metal centers through the phenanthroline linkage to form stable polypyridyl complexes. The spectral and the electrochemical characterization of Pptd complexes of Ru(II), Co(II), and Re(I) is presented.

Pptd is capable of being reduced (across the pyrazine nitrogens) by two H-atoms. When coordinated to Ru(II), Pptd forms stable complexes which retain the robust characteristics and electrochemical activity of other Ru(II) polypyridyl species. In addition, Ru(II) complexes of Pptd show pH-dependent reductions in aqueous solution. Thus, in principle, Ru(II)-Pptd complexes could be used as "H-atom transfer" mediators, capable of shuttling up to six (or more) H-atoms to suitable substrates in aqueous solution.
ACKNOWLEDGEMENT

I wish to express my sincere appreciation to Dr. Mark E. McGuire, my research advisor, for his great patience and help during this study.

Also, I would like to thank the faculty and staff of the Chemistry Department and the other members of our research group for their assistance.
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VI
INTRODUCTION

Flavins, or isoalloxazines, play an important role in almost all living organisms. They act as cofactors for flavoproteins in many metabolic redox reactions and participate as such in the respiratory chain\(^1\). The most common flavocoenzymes associated with biological materials are Rfl (riboflavin), FMN (riboflavin monophosphate) and FAD (flavin adenine dinucleotide) (Figure 1-1)\(^2\). The first flavin compound, riboflavin ("lactochrome"), was isolated from whey by Blyth in 1879\(^3\). Since then, more and more flavin compounds have been studied and developed.

Figure 1-1 (taken from ref. 2)

Various compounds involving isoalloxazine ring system

According to international recommendations, flavin is
specifically defined as 7,8-dimethylbenzo[g]-pteridine-2,4(3H,10H)-dione (Figure 1-2). In common practice, however, "flavins" refer to a class of structurally related molecules. Flavins are tricyclic molecules capable of reversible proton-coupled electron transfer reactions (H-atom transfers).

![Flavin Structure](https://via.placeholder.com/150)

**Figure 1-2**

7,8-dimethyl-benzo[g]-pteridine-2,4(3H,10H)-dione

The following example (Figure 1-3) shows how flavin (7,8-dimethyl-benzo[g]-pteridine-2,4(3H,10H)-dione) can exist in an oxidized, semi-reduced, or reduced form depending on the pH and the applied potential.

![Flavin Oxidation States](https://via.placeholder.com/150)

**Figure 1-3** (taken from ref. 2)

Oxidized, semi-reduced, and reduced flavin
Because of their chemical versatility, there has been continuing interest in the use of synthetically modified flavins as catalysts for desired organic reactions. For example, Bruice et al. found that 3,10-dimethyl-8-cyano-isoalloxazine (8-cyanoflavin) reacted with nitroalkanes to give the corresponding aldehydes. Yoneda et al. synthesized an angular "double 5-deazaflavin" which was found to oxidize cyclopentanol to cyclopentanone (apparently by hydrogen or hydride abstraction) under neutral conditions in oxygen (under a sunlamp) with a high degree of autorecycling.

Reduced flavins might be useful as H-atom donors. Some significant reactions, such as the electrochemical reduction of CO₂, require H-atom transfer in order to make them energetically feasible.

\[
\begin{align*}
\text{CO}_2 + e^- & \rightarrow \text{CO}_2^- : \quad E^0 = -2.21 \text{ V (vs. SCE)} \quad (1-1) \\
\text{CO}_2 + 2H^+ + 2e^- & \rightarrow \text{CO} + \text{H}_2\text{O} \quad E^0 = -0.52 \text{ V (vs. SCE)} \quad (1-2)
\end{align*}
\]

It is relatively easy, from a mechanistic point of view, to (continuously) reduce CO₂ by one electron (e.g. simple reduction at an electrode). However, it is energetically costly. On the other hand, reduction by two H-atoms (Equation 1-2) is much more energetically accessible, but constructing a recyclable catalyst capable of H-atom delivery presents a more difficult mechanistic challenge.

Reduction of carbon dioxide can be carried even further if more H-atoms are made available. For example:

\[
\text{CO}_2 + 4H^+ + 4e^- \rightarrow \text{HCHO} + \text{H}_2\text{O} \quad E^0 = -0.48 \text{ V (vs. SCE)} \quad (1-3)
\]
\[
\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad E^0 = -0.38 \text{ V (vs. SCE)} \quad (1-4)
\]
\[
\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad E^0 = -0.24 \text{ V (vs. SCE)} \quad (1-5)
\]

Since carbon dioxide is not easily reduced at an electrode surface (Equation 1-1), a "mediator" molecule, capable of H-atom delivery, would be useful. This mediator must be easily reduced at the electrode and must be capable of delivering multiple H-atoms to carbon dioxide.

Reduced flavins might be useful as H-atom transfer mediators for reactions such as equations 1-2 to 1-5. Flavins, however, are not always very water soluble and are not capable of transferring more than two H-atoms. This problem can be solved by finding a way to attach flavins to water soluble transition metal complexes. Several flavins could then be clustered in close proximity to one another around the metal center(s). This would make it possible to produce a H-atom transfer mediator(s) capable of delivering 2, 4, 6, 8... H-atoms to CO₂ or other potential substrates (see equations 1-2 \rightarrow 1-5).

It has been found that several metal ions (such as Ag(I), Mo(IV or V), Fe(II), and Ru(II)) can form metal-flavin complexes through coordination at the N-5 and O-4 positions of the ring\(^7\) (refer to Figure 1-1 for traditional ring numbering for flavins). However, these types of compounds are less suitable as H-atom transfer mediators since the metal attaches at one of the reactive sites on the flavin ring (N-5). A suitable flavin derivative must be one which leaves the reactive sites (N-1, N-5, C-4a, O-4) on the flavin ring open for reaction, but yet allows...
for coordination to a metal atom.

In order to meet these requirements, a new flavin isomer (an alloxazine derivative, "Pptd") has been synthesized (Figure 1-4).

\[
\text{Phen-dione} + \text{H}_2\text{N} - \text{N} - \text{H}_2\text{N} - \text{N} - \text{Ch}_3 \rightarrow \text{Pptd} + 2\text{H}_2\text{O}
\]

Figure 1-4 Pptd

This compound can be made by the condensation of 1,10-phenanthroline-5,6-dione with 5,6-diamino-1,3-dimethyluracil (Figure 1-5).

The synthesis and characterization of Pptd and several metal complexes will be described more fully in the Experimental and Results and Discussion sections.
The Pptd ligand is similar to the "flavins" discussed earlier (Figures 1-1 to 1-3) in that it contains an aromatic ring system (a phenanthroline) that is fused to a pteridine-dione ring system. In addition, Pptd should be capable of being reduced by two H-atoms (across the pyrazine N), as are alloxazine derivatives in general. The only significant difference, therefore, between Pptd and "flavin" should be in the position of reduction. In addition, Pptd fulfills the requirements stated earlier, namely, that the ligand possesses a site for metal coordination and retains the ability to be reduced by two H-atoms.

Metal ions can be used as stable "anchors" to hold one, two, or even three Pptd ligands in close proximity. Since each Pptd ligand moiety is, in principle, capable of being reduced (across the pyrazine nitrogens) by $2e^-/2H^+$ in aqueous solution, versatile electrochemical mediators could be formed (delivering at least six H-atoms). Multimetallic systems could conceivably allow attachment of more than three Pptd ligand.

The transition metal ion originally chosen for attachment of Pptd ligands was Ru(II). The reason for this choice was that, due to the nature of the bidentate linkage on Pptd, complexes with Ru(II) should closely resemble those of the well known Ru(II) polypyridine compounds. It has been found that Ru(II) polypyridine complexes (such as Ru(bpy)$_3^{2+}$ derivatives) possess the following advantages:

(1) The bidentate bipyridine-type linkages form complexes
that are very stable.

(2) Hundreds of Ru(II) polypyridine complexes have been made, and the oxidation potential of the Ru(II) complexes can be systematically varied simply by varying ligand substituents.

(3) The Ru(II) polypyridine complexes are strong light absorbers. Thus, there are many spectroscopic features which allow for straightforward characterization of the complexes.

(4) The Ru(II) polypyridine complexes are well-behaved electrochemically (easily reduced and oxidized), so they are good candidates to be electrochemical mediators.

(5) Ru(II) complexes are generally quite water soluble.

In this paper, we will describe:

(1) The synthesis and properties of the alloxazine ligand Pptd.

(2) Attachment of one, two, and three Pptd ligands to Ru(II) (and how the properties of Pptd are affected).

(3) The effect of changing the metal center (and charge) on the Pptd ligand.

(4) The pH-dependence of the reduction of Pptd coordinated to Ru(II) in aqueous solutions.
References (Chapter 1)


   (b) Bruice, T.C.; Chan, R.L. ibid, 6721.


8. Chemical Abstracts Index Name: Pteridino[6,7-f][1,10]-phenanthroline-11,13(10H,12H)-dione, 10,12-dimethyl-

EXPERIMENTAL SECTION

Materials:
Cobalt(II) chloride hexahydrate (CoCl$_2$·6H$_2$O) was a recrystallized sample obtained from Kirk Black. 1,10-Phenanthroline monohydrate (phen, 99%), potassium antimonyl tartrate hydrate (K$_2$SbT·H$_2$O, 99+%), sodium tetrafluoroborate (NaBF$_4$, 98%), ammonium hexafluorophosphate (NH$_4$PF$_6$, 99.99%), 5,6-diamino-1,3-dimethyluracil hydrate, triflic acid (CF$_3$SO$_3$H, 98%), and RuCl$_3$·xH$_2$O (3.8% H$_2$O) were obtained from Aldrich Chemical Co. and used as received. Acetonitrile (CH$_3$CN, analysis grade) was also obtained from Aldrich Chemical Co., but dried over 4A Molecular Sieves (MCB Manufacturing Chemists, Inc.). Bromine, concentrated sulfuric acid (H$_2$SO$_4$), concentrated nitric acid (HNO$_3$), disodium ethylenediaminetetraacetate dihydrate (Na$_2$EDTA·2H$_2$O), sodium carbonate (Na$_2$CO$_3$), chloroform (CHCl$_3$, reagent grade), and acetone (CH$_3$COCH$_3$) were obtained from Fisher Scientific Co. and used as received. Methanol (CH$_3$OH, reagent grade) was obtained from Fisher Scientific Co. and dried over 3A Molecular Sieves (MCB Manufacturing Chemists, Inc.). Absolute ethanol and 95% ethanol (Midwest Grain Products Co.), ethylene glycol (Eastman Kodak Co.), diethyl ether (J.T.Baker Co.), and pentane (EM Science) were used without further purification. Rhenium pentacarbonyl chloride (Re(CO)$_5$Cl) was obtained from Pressure Chemical Co. and used as received. Unless otherwise noted, all water and water solutions used house-deionized water that had passed through a Millipore Milli-Q water system equipped with a
0.22 µm filter.

**Synthesis:**

\([\text{Co}^{II}(\text{phen})_3](\text{SbT})_2\) The preparation of this complex followed a procedure similar to that reported by Lee et al\(^1\).

1,10-Phenanthroline monohydrate (13.0024 g; 6.559 x 10\(^{-2}\) moles) was placed in 600 mL of water at 80\(^0\)C. \(\text{CoCl}_2 \cdot 6\text{H}_2\text{O}\) (3.0509 g; 1.282 x 10\(^{-2}\) moles) was separately dissolved in 125 mL of hot water (80\(^0\)C). Potassium antimony tartrate hydrate (26.0083 g; 8.003 x 10\(^{-2}\) moles) was also separately dissolved in 125 mL of hot water (80\(^0\)C). The cobalt solution was added to the phenanthroline solution and stirred 10 min at 80\(^0\)C. The color turned to dark-yellowish brown. The hot antimony tartrate solution was then added to the above solution, and a yellow solid precipitated. The mixture was stirred for 10 min at 80\(^0\)C, cooled to room temperature, and then cooled further in an ice bath. The mixture was filtered on a 350 mL M frit and the solid was dried in vacuo for 5 h (yield = 15.9339 g). The solid was then extracted with acetone to remove excess phenanthroline. The solid was then dried in vacuo for 0.5 h. The final yield (15.9438 g) of \([\text{Co}^{II}(\text{phen})_3](\text{SbT})_2\) was 101.4\% (based on \(\text{CoCl}_2 \cdot 6\text{H}_2\text{O}\)). (Note: Extraction of the solid product with acetone does wash out some excess phenanthroline, as evidenced by the white crystalline material produced after evaporation of the acetone solution. It seems very odd that the final product had a higher weight than the crude solid. One possible explanation is that the solid retained an unexpected amount of water from the acetone wash.
and the short drying time was not sufficient to adequately dry the sample.)

\([\text{Co}^{III} (\text{phen})_3 ](\text{BF}_4)_3\) This complex was prepared by a method similar to that reported by Szafran et al\(^2\). Bromine (2 mL) was added to 320 mL of water while \([\text{Co}^{II} (\text{phen})_3 ](\text{SbT})_2\) (15.9438 g; 1.301 x 10\(^{-2}\) moles)\(^3\) was added to the solution. The suspension was gently refluxed for 1 h and the color changed from yellow to orange-yellow. NaBF\(_4\) (25 g; 0.2277 moles) was added to the solution while refluxing, the solution turned to reddish brown, and then all the suspended solid dissolved. The solid product was precipitated by cooling the solution in an ice bath for 2 h. The mixture was filtered on a 150 mL M frit and the orange yellow solid \([\text{Co}^{III} (\text{phen})_3 ](\text{BF}_4)_3\) was collected on a watch glass and air dried overnight. It was then dried for 5 h under vacuum. The yield (10.7403 g) of \([\text{Co}^{III} (\text{phen})_3 ](\text{BF}_4)_3\) was 97.4\% (based on CoCl\(_2\)·6H\(_2\)O). (Note: The high apparent yield was probably due to the fact that \([\text{Co}^{III} (\text{phen})_3 ](\text{BF}_4)_3\) was most likely isolated as a hydrate.)

\([\text{Co}^{III} (\text{phen-dione})_3 ](\text{PF}_6)_3\) This complex was prepared in a manner similar to that used by Gillard et al\(^4\). (Note: This reaction was always performed in a hood behind an explosion shield.) Concentrated H\(_2\)SO\(_4\) (54 mL) was placed in a 200 mL RB flask set up on a ringstand so that the contents could be stirred while being cooled in an ice bath. \([\text{Co}^{III} (\text{phen})_3 ](\text{BF}_4)_3\) (5.6844 g; 6.610 x 10\(^{-2}\) moles) was then added to the cooled H\(_2\)SO\(_4\) followed by
2.5259 g (2.5520 x 10⁻² moles) of NaBr. Some fizzing occurred when the NaBr was added. Concentrated HNO₃ (27 mL) that had been previously chilled in ice was slowly added (about 3-5 mL at a time). After the HNO₃ addition was complete, the solution was stirred in the ice bath for about 5 min. The flask was loosely stoppered with a rubber septum during this time to prevent rapid escape of an orange-brown gas (Br₂/NO₂?) but still allow for pressure relief. The ice bath was then removed, a reflux column added, and the bottom of the flask dried off. The mixture was then gently refluxed for 1 h. During this time, the mixture turned a clear dark orange-red color, and orange-red liquid condensed in the reflux column. (Caution: Care was taken not to overheat. Condensation of red liquid more than half way up the reflux column was taken as a sign of overheating.) The solution was cooled and slowly added to a stirred solution of 16.7049 g of NH₄PF₆ in 167 mL of water in a 1000 mL beaker. (The beaker was in an ice bath due to the exothermic nature of the acid dilution.) The suspension that formed was gently heated (without stirring) for about 30 min, cooled to room temperature, and then in an ice bath. Filtering the cold mixture on a 150 mL M frit gave a yellow solid ([Co⁺⁺⁺(phen-dione)₃](PF₆)₃) which was air dried.

1,10-Phenanthroline-5,6-dione (phen-dione) The isolation of phen-dione followed procedures reported by Gillard⁴. Na₂EDTA.2H₂O (4.1166 g; 1.1059 x 10⁻² moles) was placed in 167 mL of water in a 400 mL beaker and the entire sample of [Co⁺⁺⁺(phen-dione)₃](PF₆)₃
from the previous step was added to the mixture. The pH was adjusted to 5.55 by addition of solid Na₂CO₃, and the mixture changed color from yellow to dark-yellow to brown. The mixture was then transferred to a 500 mL RB flask and refluxed for 1 h. During this time, the mixture turned a dark purple-red color. After refluxing, it was cooled to room temperature and then in an ice bath. Filtering on a 150 mL M frit gave a dark-yellow solid which was washed with a few drops of cold water to remove any purple stains. The solid was then collected and air dried. The filtrate was extracted 5 times with 50 mL of chloroform each time. The combined chloroform extracts were left to evaporate in the hood. The phen-dione product was both the solid obtained from filtration and the solid left after evaporation of the chloroform extract.

The crude phen-dione was recrystallized by the following procedure. Methanol (108 mL) was put in a 200 mL RB flask equipped with a stir bar and a reflux column and heated by using a heating mantle until it was fairly warm but not refluxing, and then the crude phen-dione was added quickly. The solution was boiled for 5 min, and the hot suspension was filtered through a warm 150 M frit. The phen-dione started to come out immediately from the filtrate. The filtrate was cooled slowly on a cork-ring to room temperature, and then in an ice bath for 30 min. The mixture was filtered on a 30 mL F frit, and the solid was washed with 10 mL of cold methanol and 20 mL of ether and then dried in vacuo for 5 h. The pure phen-dione (m.p. = 259-263°C; lit.⁵ = 256-257°C) was a yellow color and the yield (1.3578 g) was 32.57% (based on [Co⁺⁺⁺(phen)₃](BF₄)₃).
pteridino[6,7-f][1,10]phenanthroline-11,13(10H,12H)-dione, 10,12-dimethyl- (Pptd)  Phen-dione (1.3578 g; 6.46 x 10⁻³ moles) from the previous step was dissolved in 100 mL of hot methanol in a 200 mL RB flask forming a yellow solution. 5,6-Diamino-1,3-dimethyluracil hydrate (1.3231 g; 7.774 x 10⁻³ moles) was dissolved in 60 mL of hot methanol in a separate 150 mL beaker. The color of the uracil solution changed from brown to yellow. The uracil solution was poured into the flask which contained the stirring phen-dione solution. The color changed from yellow to orange-red (just a few seconds) and then to a pea-green suspension. The mixture was refluxed for 1 h, cooled to room temperature, and then filtered on a 30 mL M frit. The light pea-green solid was washed twice with 5 mL of methanol and twice with 10 mL of ether and then air dried on a watch glass for 4 h (1.6853g). The crude Pptd was suspended in 200 mL of chloroform in a 500 mL beaker, stirred for 30 min, and then filtered. The filtrate (which separated from a dark green solid left in the filter) was collected in a crystallizing dish and evaporated in the hood. The yellow solid obtained (0.9625 g) was scraped out of the dish and placed in 289 mL of a 1:1 abs. ethanol/0.10 M triflic acid solution in a 500 mL RB flask equipped with a reflux column and a stir bar. The mixture was refluxed until the solid dissolved (clear yellow color). The hot solution was then filtered through a warm 60 mL M frit into a clean filter flask and slowly cooled to room temperature. The pure product precipitated and was filtered on a 30 mL F frit, washed with 10 mL of 0.10 M triflic acid, 10 mL of water, 10 mL of acetone, and 10 mL of ether.
The light-yellow solid (pure Pptd) was dried in vacuo for 5 h. The yield (0.7708 g) of Pptd was 34.6% (based on phen-dione). (Note: Earlier work\(^6\) had shown that a sample prepared by this procedure but also rigorously dried in a vacuum oven (120 °C) gave the following analysis: m.p. = 385-389 °C (decomp.). Anal. Calcd.: C, 62.79; H, 3.51; N, 24.41. Found: C, 62.80; H, 3.51; N, 24.33.) It was found that the Pptd product obtained without drying at 120 °C was suitable for synthetic purposes.

\[
((\text{bpy})\text{Ru}^{11} \text{(Pptd)}_2)(\text{PF}_6)_2 \cdot 2\text{H}_2\text{O} \quad \text{Ru(\text{bpy})Cl}_3(\text{H}_2\text{O})
\]

1.22 \times 10^{-4} moles) (Note: This compound was prepared by Jeffery W. Walk from the method of Krause et al\(^7\)) and Pptd (0.1670 g; 4.850 \times 10^{-4} moles) were mixed in 30 mL of ethylene glycol in a 100 mL RB flask equipped with a reflux column and stir bar. The mixture was refluxed until the color stopped changing (total reflux time was 1.75 h). During the reflux, the color changed from grey-green to blue-green, green, brown, orange-brown, red-orange, and finally to bright red. The mixture was cooled to room temperature, 30 mL of water was added, and then unreacted Pptd was filtered out. Solid \(\text{NH}_4\text{PF}_6\) was then added to the filtrate until precipitation was complete. The mixture was filtered and the solid was washed with 2 mL of cold water, 2 mL of cold absolute ethanol, 2 mL of chloroform, and then 5 mL of ether. The solid was collected, air dried overnight, and then dried in vacuo for 5 h. The crude \([((\text{bpy})\text{Ru}^{11} \text{(Pptd)}_2)(\text{PF}_6)_2\) was dissolved in 20 mL of acetone with stirring for 5 min and then filtered on a 15 ml F frit. Ether was
dripped into the stirring filtrate in a 100 mL beaker until a large amount of precipitate formed and the supernatant was a pale yellow color. The mixture was filtered on a 30 mL F frit, and the solid was washed with ether and dried in vacuo for 3 h. The dried solid was then redissolved in 2.5 mL of acetone and 5.0 mL of chloroform was added. Ether was dripped in (with stirring) and the product precipitated leaving a light yellow supernatant. The mixture was filtered on a 15 mL F frit, and the solid was washed with 2 mL of chloroform and then with excess ether. The orange-red solid [(bpy)Ru(II)(Pptd)₂](PF₆)₂.2H₂O was dried in vacuo for 3.5 h. The yield (0.0988 g) was 65.5% (based on Ru(II)(bpy)Cl₃(H₂O)). Anal. for [(bpy)Ru(II)(Pptd)₂](PF₆)₂.2H₂O: Calcd: C, 43.44; H, 2.85; N, 15.42. Found: C, 43.46; H, 2.92; N, 15.46.

[Ru(II)(Pptd)₃](PF₆)₂.3H₂O  RuCl₃.xH₂O (3.8% H₂O, 0.0514 g; 2.38 x 10⁻⁴ moles) and Pptd (0.3266 g; 9.48 x 10⁻⁴ moles) were mixed in 30 mL of ethylene glycol in a 100 mL RB flask equipped with a reflux column and a stir bar. The mixture was refluxed for 2 h during which the color changed from grey-green to green, brown, red-brown and finally to bright red. Solid NH₄PF₆ (0.3868 g; 2.37 x 10⁻³ moles) was added and the mixture was stirred for 5 min and then cooled to room temperature. After filtering the mixture on a 30 mL F frit, the solid was washed with 2 mL of cold water, 2 mL of cold absolute ethanol, 30 mL of chloroform, and 5 mL of ether, and then dried in vacuo for 4 h. The crude [Ru(II)(Pptd)₃](PF₆)₂ was dissolved in 25 mL of acetone and filtered on a 30 mL F frit. Ether
(about 20 mL) was slowly added to the filtrate until precipitation was complete (leaving a pale yellow supernatant). The mixture was filtered on a 15 mL F frit, the solid was washed with 2 mL of cold water, 2 mL of absolute ethanol, and 5 mL of ether, and dried in vacuo for 4 h. The dried solid was then redissolved in 20 mL of acetone and 20 mL of chloroform was added to the solution which caused precipitation of product. The mixture was filtered on a 15 mL F frit and the solid was collected and dried in vacuo for 3 h. The yield (0.1685 g) was 49.7%. Anal. for \([\text{Ru}^{11}(\text{Pptd})_3](\text{PF}_6)_2.3\text{H}_2\text{O}\): Calcd: C, 43.88; H, 2.86; N, 17.06. Found: C, 43.81; H, 3.08; N, 16.97.

Ether (about 20 mL) was added to the filtrate from the previous step causing precipitation of more product (leaving a pale yellow supernatant). The mixture was filtered on a 15 mL F frit and the solid was washed with 1 mL of chloroform, and 3 mL of ether, and then dried in vacuo for 3 h. The yield (0.0568 g) of this second recrystallization was 16.7%. Anal. for \([\text{Ru}^{11}(\text{Pptd})_3](\text{PF}_6)_2.3\text{H}_2\text{O}\): Calcd: C, 43.88; H, 2.86; N, 17.06. Found: C, 43.83; H, 3.08; N, 16.96. The solid products were combined and the total yield (0.2253 g) of \([\text{Ru}^{11}(\text{Pptd})_3](\text{PF}_6)_2.3\text{H}_2\text{O}\) was 66.5% (based on RuCl₃·xH₂O).

\([\text{Co}^{11}(\text{Pptd})_3](\text{PF}_6)_2.3\text{H}_2\text{O}\) CoCl₂·6H₂O (0.0506 g; 2.13 x 10⁻⁴ moles) and Pptd (0.3650 g; 1.060 x 10⁻³ moles) were mixed in 110 mL of 1:1 abs. ethanol/0.10 M triflic acid solution in a 250 mL RB flask equipped with a reflux column and a stir bar. The light purple color of
CoCl$_2$ disappeared quickly after Pptd was added resulting in a cloudy yellow mixture. The mixture was refluxed for 40 min. All the solid dissolved and a clear, dark yellow solution was produced. The solution was cooled to room temperature and some yellow solid came out. The solution was filtered on a 30 mL F frit. Solid NH$_4$PF$_6$ was added to the filtrate until precipitation was complete. After filtering the mixture on a 30 mL F frit, the solid was washed with 5 mL of cold water, 5 mL of cold absolute ethanol, and 5 mL of ether, and then dried in air for 3 h. The solid was dried further in vacuo for 2 h.

The dried solid was redissolved in 30 mL of acetonitrile and the resulting solution was filtered on a 30 mL F frit. (The small amount of solid produced (excess Pptd?) was then washed with 5 mL of acetonitrile, and the wash was added to the original filtrate.) Chloroform (35 mL) was added to the filtrate, and then ether (70 mL) was dripped into this solution causing precipitation. The mixture was filtered on a 30 mL F frit. The filtrate still had a light yellow color. Ether (40 mL) was dripped into this filtrate again causing precipitation, and the suspension was filtered on the same frit as used previously. The combined solids were washed with 1 mL of chloroform, and 3 mL of ether, and then dried in vacuo for 3 h. The yield (0.1257 g) was 42.8% (based on CoCl$_2$·6H$_2$O). Anal. for [Co$^{11}$\((\text{Pptd})_3\)\]\(\text{PF}_6\)\]$_2$·3H$_2$O: Calcd: C, 45.17; H, 2.95; N, 17.56. Found: C, 45.26; H, 3.01; N, 17.47.

Re$^1$(CO)$_3$(Pptd)Cl·H$_2$O  Re(CO)$_5$Cl (0.2013 g; 5.565 x 10$^{-4}$ moles) and
pptd (0.2121 g; 6.160 x 10^{-4} moles) were mixed in 250 mL of 95% ethanol in a 500 mL RB flask equipped with a reflux column and a stir bar. The mixture was refluxed for 40 min. All the solid dissolved and a clear, yellow solution was produced. The total reflux time was 1.5 h. The solution became a dark yellow color, and some yellow solid came out. The solution was hot filtered on a 30 mL M frit, and the yellow solid was saved and dried in vacuo for 5 h. The filtrate was cooled to room temperature, and more yellow solid precipitated. The mixture was filtered on a 30 mL F frit, and the yellow solid was saved and dried in vacuo for 5 h. The filtrate was evaporated in a crystallizing dish in the hood, and the yellow solid was saved and dried in vacuo for 5 h.

The first and third solids obtained were dissolved in 280 mL of chloroform in a 1000 mL beaker, and then 560 mL of n-pentane was dripped into this solution causing precipitation. The mixture was filtered on a 30 mL F frit. The solid was washed with a few drops methanol, and then dried in vacuo for 2 h. The dried yellow solid was suspended in 75 mL of hot methanol, and the mixture was cooled to room temperature and filtered on a 30 mL F frit. The solid was then dried in vacuo for 5 h. The yield (0.1827 g) was 50.51% (based on Re(CO)_5Cl). Anal. for Re^1(CO)_3(Pptd)Cl.H_2O: Calcd: C, 37.76; H, 2.11; N, 12.58. Found: C, 37.93; H, 2.20; N, 12.65.

Methods:
The pH measurements were obtained using an Orion Research Model SA230 pH meter. The melting point measurements were obtained using
either a MelTemp or a Thomas Hoover Melting Point Apparatus. Cyclic
voltammograms were obtained on a Princeton Applied Research Model
173 potentiostat connected to a Model 175 universal programmer.
Data were recorded on a Recorder Company Model 200 XY recorder.
Electrochemical experiments in either acetonitrile or
dimethylsulfoxide used 0.1M TBAH (tetra-n-butylammonium
hexafluorophosphate, Bioanalytical Systems, Inc.) as an
electrolyte. A three-electrode system consisting of a platinum disk
or glassy carbon working electrode (Bioanalytical Systems, Inc.),
a platinum-wire counter electrode and a saturated sodium chloride
calomel (SSCE) reference electrode (Bioanalytical Systems, Inc.)
were used for the cyclic voltammograms. Electronic absorption
spectra were obtained on a Shimadzu UV-3100 UV-VIS-NIR Recording
Spectrophotometer and infrared spectra were obtained on a Nicolet
20DXB FTIR Spectrometer using KBr pellets.
References (Chapter 2)


3. Due to the uncertainty in the actual weight of this compound (See text in [Co(phen)](SbT) section), the calculated number of moles used represents an upper limit.


RESULTS AND DISCUSSION

Infrared Spectra

Infrared spectra (in KBr) for Pptd and several metal-Pptd complexes are shown in Figures 3-2 to 3-9. (For comparison purposes, the spectra of 1,10-phenanthroline-5,6-dione (phen-dione), and 1,3-dimethyl-lumazine (1,3-Me₂Lum) are also included. Refer to Figure 3-1 for structural diagrams of Pptd, phen-dione, and 1,3-Me₂Lum.) The infrared spectrum (in CH₂Cl₂) for Re'(CO)₃(Pptd)Cl is shown in Figure 3-10. A summary of the carbonyl stretching frequencies for all of these compounds is found in Table 3-1.

Pptd shows two strong carbonyl absorption bands at 1676 cm⁻¹ and 1720 cm⁻¹. This seems reasonable since the two carbonyl groups (O-2 and O-4) of Pptd are in different environments. By contrast, the carbonyl stretching frequencies for the symmetric phen-dione are degenerate (1675 cm⁻¹). When the spectrum of 1,3-Me₂Lum is compared with that of Pptd, it can be seen that the carbonyl stretching frequencies of 1,3-Me₂Lum (1661 cm⁻¹ and 1715 cm⁻¹) are shifted to higher energies upon fusion of the 1,10-phenanthroline ring (to form Pptd).

The two carbonyl stretches for Pptd, 1676 cm⁻¹ and 1720 cm⁻¹ can be assigned as arising from the O-4 and O-2 positions, respectively, on the ligand (See Figure 3-1). These assignments are made based on previous measurements made on free and coordinated 1,3-Me₂Lum. When 1,3-Me₂Lum coordinates to
[(bpy)$_2$Ru$^{II}$]- to form [(bpy)$_2$Ru$^{II}$(1,3-Me$_2$Lum)](PF$_6$)$_2$, the two bands at 1661 cm$^{-1}$ and 1715 cm$^{-1}$ shift to 1624 cm$^{-1}$ and 1723 cm$^{-1}$. Since the only open bidentate coordination site on 1,3-Me$_2$Lum is at the N-5, O-4 position, Ru$^{II}$ must coordinate there and cause a large perturbation in only one of the two carbonyl stretches. Therefore, the band at 1661 cm$^{-1}$ in the free 1,3-Me$_2$Lum was assigned as the 0-4 position. Since this ligand is structurally very similar to Pptd, the lower frequency band in Pptd (1676 cm$^{-1}$) is assigned to the 0-4 position.

The carbonyl stretching frequencies for Pptd both increase by only 6 cm$^{-1}$ upon coordination to Ru(II) in the complex [(bpy)$_2$Ru$^{II}$(Pptd)](PF$_6$)$_2$.$H_2$O. This small shift in carbonyl bands is consistent with attachment of Ru(II) to the phenanthroline portion of Pptd, remote from the carbonyl sites. As the number of coordinated Pptd ligands increases from one to three, the carbonyl stretching frequencies gradually approach those of the free ligand. This is consistent with "dilution" of the effect of Ru$^{II}$ coordination.

Coordination of Pptd to cobalt(II) in the complex [Co$^{II}$(Pptd)$_3$](PF$_6$)$_2$.$3H_2$O causes the carbonyl stretching frequencies of Pptd to increase by 4 cm$^{-1}$ and 9 cm$^{-1}$ respectively. As with the series of Ru(II) complexes, the small shift in carbonyl stretching frequencies is consistent with coordination of Pptd to cobalt(II) through the phenanthroline linkage, remote from the carbonyl sites.

By comparison of the IR spectrum of [Ru$^{II}$(Pptd)$_3$](PF$_6$)$_2$.$3H_2$O
with that of \([\text{Co}^{11}(\text{Pptd})_3](\text{PF}_6)_2.3\text{H}_2\text{O}\), it can be seen that there is no shift in the Pptd carbonyl stretching frequencies for the Ru(II) complex while there is still a measurable shift in the Co(II) complex. Apparently, the effect of the +2 charge on the metal center is not as easily "diluted" in the Co(II) (d\(^7\)) complex as it is in the Ru(II) (d\(^6\)) complex. Ruthenium, a second row d-block element, is capable of undergoing significant d\(
abla\)\(\pi\) → \(\pi^*\) backbonding with polypyridyl ligands\(^2\). Perhaps this interaction, which would be absent in Co(II) complexes, is responsible for the differences in the carbonyl stretching frequencies for Pptd in \([\text{Ru}^{11}(\text{Pptd})_3](\text{PF}_6)_2.3\text{H}_2\text{O}\) and \([\text{Co}^{11}(\text{Pptd})_3](\text{PF}_6)_2.3\text{H}_2\text{O}\).

Comparison of the IR spectrum of a rhenium(I) complex of Pptd, \(\text{Re}^\dagger(\text{CO})_3(\text{Pptd})\text{Cl}\), with that of Pptd, shows that only one of the carbonyl stretching frequencies of Pptd increases by 2 cm\(^{-1}\) upon coordination to rhenium(I). This is once again consistent with coordination of Pptd through the phenanthroline linkage. It seems that rhenium(I) does not affect the carbonyl groups of Pptd, perhaps due to the low charge on the metal center. The other three IR peaks reported in Table 3-1 for \(\text{Re}^\dagger(\text{CO})_3(\text{Pptd})\text{Cl}\) are assigned as belonging to the three carbonyl groups which directly combine with rhenium(I).
Table 3-1 Carbonyl Stretching Frequencies

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v_{\text{co}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pptd</td>
<td>1676 1720</td>
</tr>
<tr>
<td>phen-dione</td>
<td>1675</td>
</tr>
<tr>
<td>$1,3$-$\text{Me}_2$Lumazine$^1$</td>
<td>1661 1715</td>
</tr>
<tr>
<td>$<a href="%5Ctext%7BPF%7D_6">\text{Co}^{\text{II}}(\text{Pptd})_3</a>_2\cdot3\text{H}_2\text{O}$</td>
<td>1680 1729</td>
</tr>
<tr>
<td>$<a href="%5Ctext%7BPF%7D_6">\text{Ru}^{\text{II}}(\text{Pptd})_3</a>_2\cdot3\text{H}_2\text{O}$</td>
<td>1677 1724</td>
</tr>
<tr>
<td>$<a href="%5Ctext%7BPF%7D_6">(\text{bpy})\text{Ru}^{\text{II}}(\text{Pptd})_2</a>_2\cdot2\text{H}_2\text{O}$</td>
<td>1680$^c$ 1725$^c$</td>
</tr>
<tr>
<td>$<a href="%5Ctext%7BPF%7D_6">(\text{bpy})_2\text{Ru}^{\text{II}}(\text{Pptd})</a>_2\cdot\text{H}_2\text{O}$</td>
<td>1682 1726</td>
</tr>
<tr>
<td>Re$^{\text{I}}$(CO)$_3$(Pptd)Cl$^a$</td>
<td>1676 1722</td>
</tr>
<tr>
<td></td>
<td>1884 1939 2034</td>
</tr>
<tr>
<td>Re$^{\text{I}}$(CO)$_3$(Pptd)Cl$^b$</td>
<td>1685 1734</td>
</tr>
<tr>
<td></td>
<td>1902 1925 2025</td>
</tr>
</tbody>
</table>

$^a$ In KBr unless otherwise noted.

$^b$ In CH$_2$Cl$_2$ solvent.

$^c$ The carbonyl stretching frequency at 1680 cm$^{-1}$ is the average of two small peaks at 1676 cm$^{-1}$ and 1684 cm$^{-1}$, and the carbonyl stretching frequency at 1725 cm$^{-1}$ shows two shoulders (1719 cm$^{-1}$ and 1734 cm$^{-1}$) around this peak.

$^d$ Spectrum recorded by K. Black.
**UV-Vis Spectra**

UV-Vis spectra for Pptd, 1,10-phen, 1,3-Me₂Lum, and the metal-Pptd complexes are shown in Figures 3-11 to 3-18. The data are summarized in Table 3-2. (Ligand structures are compared in Figure 3-1.)

By comparison of the spectrum of Pptd in acetonitrile (Figure 3-11) with that of 1,10-phenanthroline monohydrate in the same solvent (Figure 3-12), it can be seen that the peaks at 239 nm and 264 nm for Pptd are most likely $\pi \rightarrow \pi^*$ transitions arising from the phenanthroline portion of the molecule. The peaks at 380 nm and 398 nm for Pptd most likely arise from the pteridine-dione portion of the ligand. This conclusion was arrived at by comparison of the spectrum of 1,3-Me₂Lum (Figure 3-13) with that of Pptd. 1,3-Me₂Lum shows an envelope of three transitions between 324 nm and 348 nm. These transitions are red shifted in the Pptd ligand.

The spectrum of $[(bpy)_2Ru^{II}(Pptd)](PF_6)_2\cdot H_2O$ in acetonitrile is shown in Figure 3-14. Coordination of Pptd to Ru^{II} through the 1,10-phenanthroline linkage is confirmed by the presence of the characteristic MLCT (metal to ligand charge transfer) absorption band for trischelated polypyridyl Ru(II) species around 450 nm and a high-energy shoulder at 429 nm. This spectrum also shows that the peaks at 374 nm and 389 nm of the pteridine-dione portion for Pptd are blue shifted slightly in this Ru(II) complex. In addition, the UV peaks at 284 nm, 243 nm, and 209 nm are assigned as overlapping $\pi \rightarrow \pi^*$ transitions arising from the
bipyridine ligands and the 1,10-phenanthroline portion of Pptd.

Comparison of the UV-Vis spectra for the three Ru(II) complexes (Figures 3-14 to 3-16) shows that the peaks which arise from the pteridine-dione portion of Pptd do not shift in frequency as the number of Pptd ligands increases from one to three. Their intensities (absorption coefficients), however (as expected), increase linearly with the number of Pptd ligands.

The MLCT bands of the three Ru(II)-Pptd complexes provide important information about the metal-ligand interactions. For example, it was initially expected that the MLCT bands of these complexes would be at much lower energy. The reason for this is that the energies of these bands are normally fairly easy to predict for Ru(II)-polypyridyl complexes. Since the MLCT band represents oxidation of the metal center and reduction of the ligand, the lowest energy band can be estimated as the absolute difference between the measured oxidation potential of Ru$^{II}$ and the reduction potential of the most easily reduced ligand. For the complex [(bpy)$_2$Ru$^{II}$(Pptd)](PF$_6$)$_2$·H$_2$O, $E_{1/2}$(Ru$^{II/III}$) = +1.34 V and $E_{1/2}$(Pptd/Pptd$^{-}$) = -0.83 V in acetonitrile (vide infra). Thus the lowest energy MLCT for this complex (in acetonitrile) should be at an energy of 2.17 V (572 nm). The measured value (Table 3-2) is 449 nm, virtually identical to [(bpy)$_2$Ru$^{II}$(phen)](PF$_6$)$_2$. Thus, the UV-Vis spectrum of the complex [(bpy)$_2$Ru$^{II}$(Pptd)](PF$_6$)$_2$·H$_2$O seems to behave as if the pteridine-dione portion of Pptd did not exist.

Previous IR data seemed to imply, however, that some
communication between the pteridine-dione portion of Pptd and the metal center did exist. This is supported by observing (in the UV-Vis spectra) the small red shift in the MLCT bands of the Ru(II) complexes as the number of Pptd ligands increases from one to three (Table 3-2). Apparently, even though the Pptd orbitals involved in the MLCT reduction ($\pi^*$ "phenanthroline" orbitals) seem somewhat electronically separated from the Pptd orbitals involved in the electrochemical reduction ($\pi^*$ "pteridine-dione" orbitals), there is a small amount of communication between the two parts of the ligand (i.e., the electron withdrawing pteridine-dione portion of Pptd does lower the energy of the $\pi^*$ "phenanthroline" orbitals slightly, thus causing a small red shift in the MLCT band).

The spectrum of $[\text{Co}^{II}(\text{Pptd})_3](\text{PF}_6)_2.3\text{H}_2\text{O}$ in acetonitrile is shown in Figure 3-17. The spectrum shows that the Pptd peaks are blue-shifted only slightly in this Co(II) complex, and the peaks at 279 nm, 241 nm, and 207 nm are assigned as overlapping $\pi \rightarrow \pi^*$ transitions arising from the 1,10-phenanthroline portion of Pptd.

The spectrum of $\text{Re}^{I}(\text{CO})_3(\text{Pptd})\text{Cl}$ in acetonitrile is shown in Figure 3-18. The peaks at 383 nm and 399 nm are assigned as red-shifted transitions from the pteridine-dione portion of Pptd. The peaks at 281 nm, 242 nm, and 202 nm are assigned as overlapping $\pi \rightarrow \pi^*$ transitions arising from the 1,10-phenanthroline portion of Pptd. The MLCT absorption bands for $\text{Re}^{I}(\text{CO})_3(\text{phen})\text{Cl}$ ($\epsilon = 4.00 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) and $\text{Re}^{I}(\text{CO})_3(\text{phen-dione})\text{Cl}$ ($\epsilon = 3.0 \times 10^3$
M$^1\cdot$cm$^{-1}$) (in CH$_3$CN) have been observed at around 380 nm by Wrighton et al$^4$. Therefore, the MLCT absorption band for the Re$^1$(CO)$_3$(Pptd)Cl complex (expected to be ~380 nm also) is probably overshadowed by the more intense ($\epsilon = 1.28 \times 10^4$ M$^1\cdot$cm$^{-1}$) peaks from the pteridine-dione portion of Pptd.
Table 3-2 UV-Vis Spectral Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\lambda_{max}$ (nm) ($\epsilon$ in M$^{-1}$cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pptd</td>
<td>CHCl$_3$</td>
<td>402 (1.34 x 10$^4$)</td>
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<tr>
<td></td>
<td></td>
<td>383 (1.25 x 10$^4$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>273 (sh)</td>
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<td></td>
<td></td>
<td>265 (3.92 x 10$^4$)</td>
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<tr>
<td></td>
<td>CH$_3$CN</td>
<td>398, 380, 264, 239, 217</td>
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<tr>
<td>1,10-phenanthroline hydrate</td>
<td>CH$_3$CN</td>
<td>275 (sh), 263, 230, 226 (sh), 197</td>
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<tr>
<td>1,3-dimethylllumazine</td>
<td>CH$_3$CN</td>
<td>237, 324 (sh),</td>
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<tr>
<td></td>
<td></td>
<td>331, 348 (sh)</td>
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<tr>
<td><a href="PF$_6$">(bpy)$_2$Ru$^{III}$(Pptd)</a>$_2$•H$_2$O</td>
<td>CH$_3$CN</td>
<td>449 (1.75 x 10$^4$)</td>
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<td></td>
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<td>389 (1.86 x 10$^4$)</td>
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<td>374 (1.84 x 10$^4$)</td>
</tr>
<tr>
<td></td>
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<td>284 (8.40 x 10$^4$)</td>
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<td></td>
<td></td>
<td>243 (4.97 x 10$^4$)</td>
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<td>209 (4.92 x 10$^4$)</td>
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<td></td>
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<td>279 (1.07 x 10$^5$)</td>
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<tr>
<td></td>
<td></td>
<td>242 (7.69 x 10$^4$)</td>
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<td>207 (6.97 x 10$^4$)</td>
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<tr>
<td><a href="PF$_6$">Ru$^{III}$(Pptd)$_3$</a>$_2$•3H$_2$O</td>
<td>CH$_3$CN</td>
<td>454 (3.07 x 10$^4$)</td>
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<td>375 (5.13 x 10$^4$)</td>
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<td>278 (1.35 x 10$^5$)</td>
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<td></td>
<td></td>
<td>242 (1.01 x 10$^4$)</td>
</tr>
<tr>
<td></td>
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<td>208 (8.09 x 10$^4$)</td>
</tr>
</tbody>
</table>

* Go on to another page.
### Table 3-2 UV-Vis Spectral Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\epsilon$ in M$^{-1}$cm$^{-1}$</th>
<th>$\epsilon$ in M$^{-1}$cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co$^{11}$-(Pptd)$_3$(PF$_6$)$_2$·3H$_2$O</td>
<td>CH$_3$CN</td>
<td>396 (5.05 x 10$^4$)</td>
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<td>379 (4.84 x 10$^4$)</td>
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<td></td>
<td></td>
<td>302 (sh)</td>
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<td>279 (1.36 x 10$^5$)</td>
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<td>241 (9.93 x 10$^4$)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>207 (8.32 x 10$^4$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re$^{1}$(CO)$_3$(Pptd)Cl</td>
<td>CH$_3$CN</td>
<td>399 (1.26 x 10$^4$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td>383 (1.28 x 10$^4$)</td>
<td></td>
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<td></td>
<td></td>
<td>300 (sh)</td>
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<td>281 (3.68 x 10$^4$)</td>
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<td>242 (3.24 x 10$^4$)</td>
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<tr>
<td></td>
<td></td>
<td>202 (3.27 x 10$^4$)</td>
<td></td>
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</tr>
</tbody>
</table>

$^a$ Absorption coefficients determined with a single concentration.

$^b$ Due to solubility restrictions, absorption coefficients are not reported for Pptd in CH$_3$CN.

$^c$ Reference
Electrochemistry: Nonaqueous Solutions

Cyclic voltammograms of Pptd and its metal complexes in nonaqueous solutions are shown in Figures 3-19 to 3-24. A summary of the electrochemical data is presented in Table 3-3.

The cyclic voltammogram of [(bpy)$_2$Ru$^{II}(Pptd)$](PF$_6$)$_2$.H$_2$O in acetonitrile is shown in Figure 3-20. A single, nearly reversible ($\Delta E_p = 70$ mV) wave was observed at $E_{1/2} = +1.34$ V (vs. SSCE). The $E_{1/2}$ of +1.34 V for the complex is in the region expected for one-electron metal-centered oxidations of [(bpy)$_2$Ru$^{II}(LL)$]$^{2+}$ compounds where LL = a heterocyclic ring$^2$. This wave is therefore assigned as a one-electron oxidation of the Ru$^{II}$ center in the complex.

Comparison of the $E_{1/2}$(Ru$^{III}$/Ru$^{II}$) of [Ru$^{II}$(bpy)$_3$](PF$_6$)$_2$$^5$ with that of [(bpy)$_2$Ru$^{II}(Pptd)$](PF$_6$)$_2$.H$_2$O (both in acetonitrile) shows that [(bpy)$_2$Ru$^{II}(Pptd)$](PF$_6$)$_2$.H$_2$O ($E_{1/2} = +1.34$ V) is harder to oxidize than [Ru$^{III}$(bpy)$_3$](PF$_6$)$_2$ ($E_{1/2} = +1.29$ V). This is consistent with the pteridine-dione portion of Pptd exhibiting a small, but measurable effect on the Ru$^{II}$ metal center.

In acetonitrile, all three Ru(II) complexes (with one to three Pptd ligands) exhibited fairly reversible ($\Delta E_p = 74-80$ mV) oxidations typical of the one-electron metal-centered oxidations of Ru(II) polypyridyl species$^2$. It can be seen that the $E_{1/2}$ values for the metal-centered oxidations (Table 3-3) increase smoothly with the number of Pptd ligands. This data, along with the small shifts in the MLCT transitions and Pptd C=O stretching frequencies, once again indicate that electronic isolation of the
pteridine-dione orbitals from Ru(II), while severe, is not total.

The cyclic voltammogram for [(bpy)$_2$Ru$^{II}$ (Pptd)](PF$_6$)$_2$.H$_2$O in acetonitrile (Figure 3-20) also shows two ligand-based reductions which have been assigned as arising from the pteridine-dione portion of Pptd ($E_{1/2} = -0.83$ V) and one of the bipyridines ($E_c = -1.40$ V). This assignment is consistent with that previously reported for [(bpy)$_2$Ru$^{II}$(dppz)]$^{2+}$ (dppz = dipyrido-[3,2-a:2',3'-c]phenazine; structure in Figure 3-1) in dry DMF. The Pptd reduction wave contains what is presumably an adsorption pre-wave (its presence or absence seems to depend on the history of the electrode and/or solution), and the bipyridine reduction does not appear to be reversible in acetonitrile.

The number of electrons involved in an electrochemical process is proportional to the area under the oxidation/reduction curves in the cyclic voltammogram (CV). In Figure 3-20, it appears that the reduction of Pptd ($E_{1/2} = -0.83$ V), and the oxidation of the Ru(II) center ($E_{1/2} = +1.34$ V) both have CV peak areas that are approximately equal. Since the oxidation at $E_{1/2} = +1.34$ V can be unequivocally assigned as a one-electron process, the Pptd reduction is also assigned as a one-electron reaction.

As mentioned in the Introduction, the Pptd ligand should be capable of being reduced by two H-atoms.
These processes demand $H^+$ ions, which are readily available in aqueous solutions. (The reduction of $[(bpy)_2Ru^{II}(Pptd)]^{2+}$ in aqueous environments will be discussed later.) However, in nonaqueous environments, such as acetonitrile, the lack of readily available $H^+$ ions could force the Pptd ligand to accept one-electron reduction.

Consistent with this analysis, reduction of coordinated Pptd in $[(bpy)_2Ru^{II}(Pptd)]^{2+}$ appears to be a one-electron process in acetonitrile (Figure 3-20). On the other hand, in aqueous solutions, Pptd reduction appears to be multielectron, occurs at less negative potentials than in acetonitrile, and is pH-dependent. (vide infra.)

Cyclic voltammograms (reductions) for both free Pptd and the three Ru(II) complexes were also taken in dimethylsulfoxide. The reason for this was that dimethylsulfoxide was the only solvent.
found that would sufficiently dissolve both free Pptd and the metal complexes. (This allowed comparison of the reduction potential of free and coordinated Pptd. Also, the ligand based reductions for the metal complexes appeared more well-behaved in dimethylsulfoxide, as opposed to acetonitrile.)

The CV for free Pptd in dimethylsulfoxide is shown in Figure 3-19. Although possibly complicated by adsorption phenomena, it is clear that free Pptd is reduced at around -0.84 V (vs. SSCE) in this nonaqueous environment. When Pptd is coordinated to Ru$^{II}$ in [(bpy)$_2$Ru$^{II}$Pptd]$^{2+}$ however, the Pptd reduction occurs at a less negative potential ($E_{1/2} = -0.74$ V). This once again demonstrates that the pteridine-dione portion of Pptd (the site of electrochemical reduction) does sense the presence of the Ru$^{II}$ center.

Reductive scans of the three Ru(II) complexes with one, two, three Pptd ligands are compared in dimethylsulfoxide in Figure 3-21. It can be seen that both [(bpy)$_2$Ru$^{II}$Pptd]$^{2+}$ and [(bpy)Ru$^{II}$Pptd]$_2$$^{2+}$ show reductive waves at around -1.3 V which are assigned as being due to one-electron reduction of a bipyridine ligand. The absence of this peak in [Ru$^{II}$Pptd]$_3$$^{2+}$ is consistent with this assignment. In addition, it can be seen that one, two, and three reduction waves are observed in the range of -0.72 V to -0.93 V for the complexes with one, two, and three Pptd ligands, respectively. Except for [(bpy)$_2$Ru$^{II}$Pptd]$^{2+}$ (for which $E_{1/2}$ (1) = -0.74 V and $E_{1/2}$ (2) = -1.26 V) the ligand-based reductions did not show good reversibility in dimethylsulfoxide.
Figure 3-22 shows the CV of $[\text{Co}^{\text{II}}(\text{Pptd})_3]^{2+}$ in acetonitrile. The oxidation wave centered at $E_{1/2} = +0.53$ V has been assigned as a one-electron oxidation of the Co(II) center. This compares to $E_{1/2} = +0.34$ to $+0.36$ V for $[\text{Co}^{\text{II}}(\text{bpy})_3]^{2+}$ and $E_{1/2} = +0.38$ to $+0.39$ V for $[\text{Co}^{\text{II}}(\text{phen})_3]^{2+}$, also in acetonitrile. The 0.14 to 0.19 V positive shift in oxidation potential for $[\text{Co}^{\text{II}}(\text{Pptd})_3]^{2+}$ could only be due to the the electron-withdrawing pteridine-dione portion of Pptd. This shift in $E_{1/2}$ is slightly larger than that discussed earlier for $[\text{Ru}^{\text{II}}(\text{Pptd})_3]^{2+}$ ($E_{1/2} = +1.42$ V for $[\text{Ru}^{\text{II}}(\text{Pptd})_3]^{2+}$ versus $E_{1/2} = +1.29$ V for $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$). This larger shift for the Co(II) complexes is consistent with what was observed earlier in the IR spectrum. (The shift in C=O stretching frequency for coordinated vs free Pptd was larger for the $[\text{Co}^{\text{II}}(\text{Pptd})_3]^{2+}$ than for the $[\text{Ru}^{\text{II}}(\text{Pptd})_3]^{2+}$.) This would mean that the interaction between Co(II) and Pptd is more pronounced than between Ru(II) and Pptd. However, this argument can not be pressed too vigorously based on the electrochemical data since the error in $E_{1/2}$ determination is most likely in the 20 to 30 mV range.

Figure 3-23 compares the reductive scans of $[\text{Ru}^{\text{II}}(\text{Pptd})_3]^{2+}$ and $[\text{Co}^{\text{II}}(\text{Pptd})_3]^{2+}$ in acetonitrile. The voltammograms appear to be complicated. However, from a comparison of the reduction of Pptd in $[\text{Co}^{\text{II}}(\text{Pptd})_3]^{2+}$ with the first reduction of Pptd in $[\text{Ru}^{\text{II}}(\text{Pptd})_3]^{2+}$ it can be seen that Pptd in the Co(II) complex is slightly harder to reduce than in the Ru(II) complex.

Figure 3-24 shows the CV of $\text{Re}^{\text{I}}(\text{CO})_3(\text{Pptd})\text{Cl}$ in
acetonitrile. The oxidation wave at $E_{pa} = +1.40$ V has been assigned as one-electron oxidation of the Re(I) center. This compares to $E_{pa} = +1.35$ V$^{10}$ for Re$^I$(CO)$_3$(bpy)Cl and $E_{pa} = +1.33$ V$^{10}$ for Re$^I$(CO)$_3$(phen)Cl. The 0.05 to 0.07 V positive shift in oxidation potential for Re$^I$(CO)$_3$(Pptd)Cl must then be due to the electron-withdrawing pteridine-dione portion of Pptd.

A comparison of reductive scans of both [((bpy)$_2$Ru$^{II}$(Pptd))]$^{2+}$ and Re$^I$(CO)$_3$(Pptd)Cl in acetonitrile (Figures 3-20 and 3-24, respectively) reveals that coordinated Pptd is slightly harder to reduce in the Re(I) complex. The second reduction in the Re(I) complex ($E_{1/2} = -1.51$ V) does not represent reduction of a polypyridyl ligand, as in Ru(II), but rather reduction of Re(I) to Re(0). This second metal-centered reduction in Re$^I$(CO)$_3$(Pptd)Cl is more negative than in Re$^I$(CO)$_3$(bpy)Cl ($E_{1/2} = -1.41$ V)$^{10}$ due to the fact that the former represents reduction of a (-1) to a (-2) species, while that of the latter is (0) to (-1).
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$E_{1/2}$ (V)</th>
<th>$\Delta E_p$ (mV)</th>
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<tbody>
<tr>
<td>Pptd</td>
<td>DMSO</td>
<td>$-0.84$ (130)</td>
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<tr>
<td>[(bpy)$_2$Ru$^{II}$([Pptd])($PF_6$)$_2$.H$_2$O</td>
<td>CH$_3$CN</td>
<td>$+1.34$ (75)</td>
<td>$-0.83$ (100), $-1.40^d$</td>
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<td></td>
<td>DMSO</td>
<td>$-0.74$ (75), $-1.26$ (80)</td>
<td>$-1.12$</td>
</tr>
<tr>
<td>[(bpy)Ru$^{II}$([Pptd])$_2$($PF_6$)$_2$.2H$_2$O</td>
<td>CH$_3$CN</td>
<td>$+1.39$ (75)</td>
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<tr>
<td></td>
<td>DMSO</td>
<td>$-0.78^c$, $-0.93^c$, $-1.32^d$</td>
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<tr>
<td>[Ru$^{II}$([Pptd])$_3$($PF_6$)$_2$.3H$_2$O</td>
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<td>$+1.42$ (80)</td>
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<tr>
<td></td>
<td>DMSO</td>
<td>$-0.72^d,e$, $-0.80^d$, $-0.93^d$</td>
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<td>CH$_3$CN</td>
<td>$+0.53$ (80)</td>
<td>$-0.75^d$</td>
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<tr>
<td>Re$^I$(CO)$_3$(Pptd)Cl</td>
<td>CH$_3$CN</td>
<td>$+1.40^f$</td>
<td>$-0.87$ (80), $-1.51$ (90)</td>
</tr>
</tbody>
</table>

- **Pt working electrode,** **Pt auxilliary electrode,** **SSCE reference electrode. All solutions purged with N$_2$ prior to use.** $E_{1/2} = (E_c + E_p)/2$; $\Delta E_p = E_{pc} - E_{pa}$ (in mV); $E_{pc}$ and $E_{pa}$ = peak potentials for reduction and oxidation, respectively.  
- **Electrolyte:** 0.1 M tetrabutylammonium hexafluorophosphate (TBAH).  
- **$E_{pc}$ values only.**  
- **Irreversible reduction.**  
- **The peak at $-0.72$ V, which is often seen as a shoulder on the broad peak at $-0.80$ V, was, depending on the history of the electrode, occasionally more distinct.**  
- **Irreversible oxidation.**
Electrochemistry: Aqueous Solutions

It was stated in the Introduction that one of the main reasons for synthesizing metal complexes of Pptd was to investigate their ability to act as H-atom transfer mediators in aqueous solutions. The ability of coordinated Pptd ligands to act as H-atom transfer mediators depends on their tendency to undergo facile proton-coupled reductions at electrode surfaces. This section will present the results of the reduction of Pptd coordinated to Ru(II) in aqueous solution.

Figure 3-25 shows the cyclic voltammogram of \[(\text{bpy})_2\text{Ru}^{II}(\text{Pptd})\] in pH = 4.32 phosphate buffer. The metal-centered oxidation \((E_{1/2} = +1.11 \text{ V}, \Delta E_p = 70 \text{ mV})\) and the Pptd-centered reduction \((E_{1/2} = -0.52 \text{ V}, \Delta E_p = 100 \text{ mV})\) are both easier to accomplish in aqueous solution than in acetonitrile. The oxidation of the Ru(II) complex is easier in aqueous solution than in acetonitrile presumably because of the higher dielectric constant of water \((\epsilon_0 = 80.1 \text{ vs } 37.05)\). The reduction of coordinated Pptd in the Ru(II) complex is easier in aqueous solution than in acetonitrile due to the ready availability of hydrogen ions in the buffer. Equation 3-1 showed the expected stoichiometry for reduction of Pptd in aqueous solution \((2e^-/2H^+ \text{ reduction})\). A comparison of the relative peak areas for Pptd reduction and the one-electron Ru(III/II) couple in Figure 3-25 is consistent with \(2e^-\) reduction of Pptd.

The involvement of \(H^+\) ions in Pptd reduction can be investigated by observing the pH-dependence of the process.
For the reaction: $\text{RuP}^{2+} + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{RuPH}^2^+$

($\text{RuP}^{2+} = [(\text{bpy})_2\text{Ru}^{11}\text{(Pptd)}]^{2+}$, $\text{RuPH}^2^+ = [(\text{bpy})_2\text{Ru}^{11}\text{(PptdH}_2\text{)}]^{2+}$),

the Nernst equation $^{12}$ could be written as:

$$ E = E^0 - \frac{0.059\text{ V}}{2} \log\left(\frac{[\text{RuPH}^{2+}]}{[\text{RuP}^{2+}][\text{H}^+]^2}\right) $$

or

$$ E = E^0 - \frac{0.059\text{ V}}{2} \log[\text{RuPH}^{2+}] + \frac{0.059\text{ V}}{2} \log[\text{RuP}^{2+}] + 0.059\text{ V} \log[\text{H}^+] $$

$$ = E^0 + C + 0.059\text{ V} \log[\text{H}^+] $$

$$ = C' - 59 \text{ mV x pH} \tag{3-4} $$

That is, for a $2\text{e}^-/2\text{H}^+$ process, the reduction potential becomes more negative by 59 mV for each unit increase in pH.

Figure 3-26 and Table 3-4 show that, from pH = 1.05 to around pH = 6.6, the measured $E_{1/2}$ for reduction of Pptd decreases by around 59 mV/pH unit. (The line drawn through the data in Figure 3-25 from pH = 1.05 to pH = 6.6 is a "forced fit" of slope 0.059 V/pH unit.) This data, along with the previously mentioned peak area data in Figure 3-25 are consistent with reduction of coordinated Pptd in $[(\text{bpy})_2\text{Ru}^{11}\text{(Pptd)}]^{2+}$ by 2 H-atoms ($2\text{e}^-/2\text{H}^+$).

As can be observed in Figure 3-26, the slope of the pH-dependence seems to change at higher pH. At higher pH values, the availability of $\text{H}^+$ ions continues to decrease, and the reduction of coordinated Pptd may be expected to involve only one or (at high pH) no $\text{H}^+$ ions. For example, at intermediate pH values, the
reduction might occur as:

\[
\text{RuP}^{2+} + 2\text{e}^- + \text{H}^+ \rightarrow \text{RuPH}^+
\]

Solving the Nernst equation for this process gives:

\[
E = E^0 + C + \frac{-\log[H]^+}{2} = C' - 30 \text{ mV} \times \text{pH} \quad \text{(3-5)}
\]

Thus, for this process, the plot of \(E_{1/2}\) vs \(\text{pH}\) would be expected to show a slope of 30 mV/pH unit. Moreover, at high \(\text{pH}\),

\[
\text{RuP}^{2+} + 2\text{e}^- \rightarrow \text{RuP}
\]

The Nernst equation for this process gives:

\[
E = C' \quad \text{(no pH dependence)} \quad \text{(3-6)}
\]

Figure 3-26 shows a "forced-fit" line of slope 30 mV/pH unit from around \(\text{pH} = 6.6\) to \(\text{pH} = 8.4\), and a line of zero slope at \(\text{pH} > 8.4\). These two lines, along with the original line of slope 59 mV/pH unit, appear to give a reasonable fit to the observed data. The CV data for reduction of Pptd in \([(\text{bpy})_2\text{Ru}^{II}(\text{Pptd})]^2+\) is therefore consistent with the following scheme:

\[
\begin{align*}
\text{pH} = 1.05 \text{ to } 6.6 \\
[(\text{bpy})_2\text{Ru}^{II}(\text{Pptd})]^2+ + 2\text{e}^- + 2\text{H}^+ & \rightarrow [(\text{bpy})_2\text{Ru}^{II}(\text{PptdH}_2)]^2+ \quad \text{(3-7)} \\
\text{pH} = 6.6 \text{ to } 8.4 \\
[(\text{bpy})_2\text{Ru}^{II}(\text{Pptd})]^2+ + 2\text{e}^- + \text{H}^+ & \rightarrow [(\text{bpy})_2\text{Ru}^{II}(\text{PptdH})]^+ \quad \text{(3-8)} \\
\text{pH} = 8.4 \text{ to } 10.0 \\
[(\text{bpy})_2\text{Ru}^{II}(\text{Pptd})]^2+ + 2\text{e}^- & \rightarrow [(\text{bpy})_2\text{Ru}^{II}(\text{Pptd})]^0 \quad \text{(3-9)}
\end{align*}
\]

The points of intersection of the lines of different slopes
on the $E_{1/2}$ vs pH diagram give estimations of the $pK_a$ values of the reduced Pptd ligand in $[(bpy)_2Ru^{II}(Pptd)]^{2+}$. For example, the intersection points in Figure 3-26 are at pH = 6.6 and 8.4. These represent $pK_{a1}$ and $pK_{a2}$ of the 2e$^-$-reduced complex. Thus:

$[(bpy)_2Ru^{II}(PptdH_2)]^{2+} \rightarrow [(bpy)_2Ru^{II}(PptdH)]^{+} + H^+$ \hspace{1cm} (3-10)

$pK_{a1} = 6.6$

$[(bpy)_2Ru^{II}(PptdH)]^{+} \rightarrow [(bpy)_2Ru^{II}(Pptd)]^{0} + H^+$ \hspace{1cm} (3-11)

$pK_{a2} = 8.4$

Plots of $E_{1/2}$ vs pH were also constructed from data obtained on the reduction of Pptd ligands in $[(bpy)Ru^{II}(Pptd)]^{2+}$ and $[Ru^{II}(Pptd)_3]^{2+}$. Since these complexes involve multiple Pptd ligands, it might be expected that their pH-dependent reductions would (or could) be quite complex. However, it was found that, within the precision of the $E_{1/2}$ vs pH plots, both $[(bpy)Ru^{II}(Pptd)]^{2+}$ and $[Ru^{II}(Pptd)_3]^{2+}$ showed three pH-dependence "zones" very similar to $[(bpy)_2Ru^{II}(Pptd)]^{2+}$.

For example, the $E_{pc}$ vs pH plot for $[(bpy)Ru^{II}(Pptd)]^{2+}$ (Figure 3-27) shows a "forced-fit" line of slope 59 mV/pH unit from pH = 1.05 to around pH = 5.9, a "forced-fit" line of slope 30 mV/pH from around pH = 5.9 to pH = 7.9, and a line of zero slope at pH > 7.9. These three lines appear to give a reasonable fit to the observed data. The CV data for reduction of both Pptd ligands in $[(bpy)Ru^{II}(Pptd)]^{2+}$ is thus consistent with $4e^-/4H^+$ reduction (pH = 1.05 to 5.9), followed by $4e^-/2H^+$ reduction (pH = 5.9 to 7.9), and $4e^-$ reduction (pH > 7.9).
\[ \text{pH} = 1.05 \text{ to } 5.9 \]
\[ [(\text{bpy})\text{Ru}^{11}(\text{Pptd})_2]^2+ + 4e^- + 4H^+ \rightarrow [(\text{bpy})\text{Ru}^{11}(\text{PptdH}_2)_2]^2+ \] (3-12)

\[ \text{pH} = 5.9 \text{ to } 7.9 \]
\[ [(\text{bpy})\text{Ru}^{11}(\text{Pptd})_2]^2+ + 4e^- + 2H^+ \rightarrow [(\text{bpy})\text{Ru}^{11}(\text{PptdH})_2]^0 \] (3-13)

\[ \text{pH} = 7.9 \text{ to } 10.0 \]
\[ [(\text{bpy})\text{Ru}^{11}(\text{Pptd})_2]^2+ + 4e^- \rightarrow [(\text{bpy})\text{Ru}^{11}(\text{Pptd})_2]^2^- \] (3-14)

In a similar manner to \([(\text{bpy})_2\text{Ru}^{11}(\text{Pptd})]^2+\), the Nernst equation for reduction of \([(\text{bpy})\text{Ru}^{11}(\text{Pptd})_2]^2+\) would predict the above scheme if the Pptd ligands acted independently.

For example:

\[ \text{RuP}_2^{2+} + 4e^- + 4H^+ \rightarrow \text{Ru}(\text{PH}_2)_2^{2+} \]

\[ E = E^0 - \frac{0.059V}{4} \log \frac{[\text{Ru}(\text{PH}_2)_2^{2+}]}{[\text{RuP}_2^{2+}][\text{H}^+]^4} \]

\[ = E^0 - \frac{0.059V}{4} \log \frac{[\text{Ru}(\text{PH}_2)_2^{2+}]}{[\text{RuP}_2^{2+}]} + \frac{0.059V}{4} \log [\text{H}^+] \]

\[ = E^0 + C + 0.059V \log [\text{H}^+] \]

\[ = C' - 59 \text{ mV} \times \text{pH} \]

This result is identical to equation 3-4 for a \(2e^-/2H^+\) process. In a similar manner, \(4e^-/2H^+\) reduction would show a slope of 30 mV/pH unit in an \(E\) vs pH plot, and \(4e^-\) reduction would be pH-independent.

\(E_{1/2}\) vs pH plot for \([\text{Ru}^{11}(\text{Pptd})_3]^2+\) (Figure 3-28) also shows evidence of the three Pptd ligands acting independently. A
reasonable fit is obtained by using a "forced-fit" line of slope 59 mV/pH unit from pH = 1.05 to around pH = 7.2, a "forced-fit" line of 30 mV/pH unit from around pH = 7.2 to pH = 8.6, and a line of zero slope at pH > 8.6. Using the Nernst equation in a manner similar to that used for the other two complexes, the CV data for reduction of Pptd in [Ru\textsuperscript{II}(Pptd)\textsubscript{3}]\textsuperscript{2+} can be shown to be consistent with the following scheme:

\textbf{pH = 1.05 to 7.2}

\[ \text{[Ru}^{\text{II}}(\text{Pptd})_3\text{]}^{2+} + 6e^- + 6H^+ \rightarrow \text{[Ru}^{\text{II}}(\text{PptdH}_2)_3\text{]}^{2+} \quad (3-15) \]

\textbf{pH = 7.2 to 8.6}

\[ \text{[Ru}^{\text{II}}(\text{Pptd})_3\text{]}^{2+} + 6e^- + 3H^+ \rightarrow \text{[Ru}^{\text{II}}(\text{PptdH})_3\text{]}^- \quad (3-16) \]

\textbf{pH = 8.6 to 10.0}

\[ \text{[Ru}^{\text{II}}(\text{Pptd})_3\text{]}^{2+} + 6e^- \rightarrow \text{[Ru}^{\text{II}}(\text{Pptd})_3\text{]}^{4-} \quad (3-17) \]

It might be expected that the pK\textsubscript{a1} and pK\textsubscript{a2} values for reduced Pptd in these Ru\textsuperscript{II} complexes (summarized in Table 3-7) could be used to compare the extent of electronic communication between Pptd and Ru(II) in the three complexes. However, given the estimated uncertainty in these pK\textsubscript{a} values (±0.5 units), there is essentially no difference between any of the values. This is not surprising, however, given the fact that the three Pptd ligands in [Ru\textsuperscript{II}(Pptd)\textsubscript{3}]\textsuperscript{2+}, for example, seem to act quite independently. In addition, any slight interaction between Pptd and the metal centers (which can be measured with the more sensitive IR and UV-Vis techniques) would probably not be measurable in the pH-dependence experiments due to the low
precision of the measurements and of the graphing techniques.
Table 3-4. \([\text{(bpy)}_2\text{Ru}^{11}\text{(Pptd)}](\text{PF}_6)_2\cdot\text{H}_2\text{O}\)

<table>
<thead>
<tr>
<th>Medium</th>
<th>pH</th>
<th>(E_{1/2}^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10 M triflic acid</td>
<td>1.05</td>
<td>-0.320 V</td>
</tr>
<tr>
<td>0.01 M (\text{H}_2\text{SO}_4/0.10\ M \text{Na}_2\text{SO}_4)</td>
<td>2.26</td>
<td>-0.394 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>3.32</td>
<td>-0.464 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>4.30</td>
<td>-0.518 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>5.32</td>
<td>-0.568 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>5.80</td>
<td>-0.595 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>6.20</td>
<td>-0.618 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>6.75</td>
<td>-0.650 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>7.33</td>
<td>-0.672 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>8.00</td>
<td>-0.685 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>8.75</td>
<td>-0.709 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>9.34</td>
<td>-0.695 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>10.00</td>
<td>-0.695 V</td>
</tr>
</tbody>
</table>

\(^a\) \(E_{1/2} = (E_{pc} + E_{pa})/2\)

Table 3-5. \([\text{(bpy)}\text{Ru}^{11}\text{(Pptd)}_2](\text{PF}_6)_2\cdot\text{H}_2\text{O}\)

<table>
<thead>
<tr>
<th>Medium</th>
<th>pH</th>
<th>(E_{p/2}^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10 M triflic acid</td>
<td>1.05</td>
<td>-0.305 V</td>
</tr>
<tr>
<td>0.01 M (\text{H}_2\text{SO}_4/0.10\ M \text{Na}_2\text{SO}_4)</td>
<td>2.38</td>
<td>-0.380 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>3.32</td>
<td>-0.435 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>4.30</td>
<td>-0.490 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>5.23</td>
<td>-0.540 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>5.70</td>
<td>-0.560 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>6.20</td>
<td>-0.585 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>6.70</td>
<td>-0.605 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>7.00</td>
<td>-0.615 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>7.33</td>
<td>-0.625 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>7.70</td>
<td>-0.635 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>8.33</td>
<td>-0.640 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>8.80</td>
<td>-0.640 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>9.26</td>
<td>-0.645 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>10.00</td>
<td>-0.645 V</td>
</tr>
</tbody>
</table>

\(^b\) \(E_{p/2}\) is a potential at half curve of the peak.
### Table 3-6. \([\text{Ru}^{11}\text{Pptd})_3](\text{PF}_6)_2\cdot3\text{H}_2\text{O}\)

<table>
<thead>
<tr>
<th>Medium</th>
<th>pH</th>
<th>(E_{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10 M triflic acid</td>
<td>1.05</td>
<td>-0.305 V</td>
</tr>
<tr>
<td>0.01 M (\text{H}_2\text{SO}_4)/0.10 M (\text{Na}_2\text{SO}_4) phosphate</td>
<td>2.38</td>
<td>-0.368 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>3.32</td>
<td>-0.420 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>4.30</td>
<td>-0.478 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>5.23</td>
<td>-0.538 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>5.70</td>
<td>-0.578 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>6.20</td>
<td>-0.602 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>6.80</td>
<td>-0.640 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>7.30</td>
<td>-0.665 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>7.80</td>
<td>-0.682 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>8.30</td>
<td>-0.692 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>8.80</td>
<td>-0.700 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>9.26</td>
<td>-0.695 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>9.65</td>
<td>-0.708 V</td>
</tr>
<tr>
<td>phosphate</td>
<td>10.00</td>
<td>-0.705 V</td>
</tr>
</tbody>
</table>

### Table 3-7 pKₘ Values of Reduced Ru⁺⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻

<table>
<thead>
<tr>
<th>Complex</th>
<th>(pK_{m1})</th>
<th>(pK_{m2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(<a href="%5Ctext%7BPF%7D_6">\text{bpy})_2\text{Ru}^{11}\text{Pptd})_2</a>_2\cdot\text{H}_2\text{O})</td>
<td>6.6</td>
<td>8.4</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BPF%7D_6">\text{bpy})\text{Ru}^{11}\text{Pptd})_2</a>_2\cdot2\text{H}_2\text{O})</td>
<td>5.9</td>
<td>7.9</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BPF%7D_6">\text{Ru}^{11}\text{Pptd})_3</a>_2\cdot3\text{H}_2\text{O})</td>
<td>7.2</td>
<td>8.6</td>
</tr>
</tbody>
</table>
Figure 3-1
Structures of Pptd and related ligands
References (Chapter 3)


SUMMARY

A pteridine-dione has been fused to a 1,10-phenanthroline to form the Pptd ligand. The Pptd ligands attach to Ru(II), Co(II), or Re(I) metal centers through the phenanthroline linkage. This is supported by both spectral and electrochemical data. The Pptd, while coordinated to Ru(II), dissolves in aqueous solutions and undergoes pH-dependent reductions. The design of the ligand allows the synthesis of Ru(II) complexes that exhibit pH-dependent reductions but yet appear to retain the traditional stability and characteristics of Ru(II) polypyridyl complexes. Such complexes may be useful as electrochemical mediators, acting as H-atom transfer agents.

Future research work will revolve around the synthesis of bi- and trimetallic complexes with up to six coordinated Pptd ligands. In addition, synthesis of an isoalloxazine derivative of Pptd is also planned. Finally, incorporation of Pptd complexes into polymers coated on electrodes (modified electrodes showing pH-dependent behavior) will be explored.
Figure 3-3 IR spectrum of phen-dione (KBr)
Figure 3-4 IR spectrum of 1,3-Me₂Lum (KBr)
Figure 3-5 IR spectrum of $[\text{Co}^{\text{II}}(\text{Pptd})_3](\text{PF}_6)_2\cdot3\text{H}_2\text{O}$ (KBr)
Figure 3-8 IR spectrum of [(bpy)$_2$Ru$^{II}$]$(Pptd)]$(PF_6)_2\cdot H_2O$ (KBr)

CO stretch: (4 cm$^{-1}$ res.)

1682 cm$^{-1}$

1726 cm$^{-1}$
Figure 3-10 IR spectrum of Re¹(CO)₃(Pptd)Cl.H₂O (CH₂Cl₂)
Figure 3-11 UV-Vis spectrum of Pt complexes in CH₃CN

λₘₐₓ = 239, 263.5 (sh), 273, 380, 396
Figure 3-12 UV-Vis spectrum of 1,10-phen (CH$_3$CN)
Figure 3-14 UV-Vis spectrum of [(bpy)$_2$Ru$_{2}^{II}$ (Ptd)$_4$](PF$_6$)$_2$·H$_2$O (CH$_3$CN)
Figure 3-15 UV-Vis spectrum of [(bpy)RuII(Pptd)2](PF6)2·2H2O (CH3CN)
Figure 3-16 UV-Vis spectrum of [Ru^{II}(Pptd)_3](PF_6)_2·3H_2O (CH_3CN)
Figure 3-17 UV-Vis spectrum of [Co(u)(PAct)](PF$_6$)$_2$·3H$_2$O (CH$_3$CN)
Figure 3-18 UV-Vis spectrum of Re\(_2\)(CO)\(_6\)(PPTd)_2Cl\(_2\).H\(_2\)O (CH\(_3\)CN)
Figure 3-19 Cyclic voltammogram of Pptd (DMSO)
Figure 3-20 Cyclic voltammogram of [(bpy)_2Ru^{II}(Pptd)](PF_6)_2·H_2O (CH_3CN)
Figure 3-21 Cyclic voltammograms (reductive scans) for three Ru(II)-Pptd complexes (DMSO)

Platinum
100 mV/sec

n=1

$E_{1/2} = -0.76\text{V}$

$E_{1/2} = -0.76\text{V}$

n=2

$E_{1/2} = -0.80\text{V}$

n=3

$E_{1/2} = -0.94\text{V}$

$E_{1/2} = -0.95\text{V}$
Figure 3-22 Cyclic voltammogram of [Co$^{II}$](Pptd)$_2$]PF$_6$•2·3H$_2$O (CH$_3$CN)
Figure 3-23 Cyclic voltammograms (reductive scans) for

\([\text{Ru}^{II}(\text{Pptd})_3]^{2+}\) (A) and \([\text{Co}^{II}(\text{Pptd})_3]^{2+}\) (B) (CH\(_3\)CN)
Figure 3-24 Cyclic voltammogram of Re(CO)$_3$(Ptd)Cl.H$_2$O (CH$_3$CN)

Volt vs SCE
Volts vs SSCE

Figure 3-25 Cyclic voltammogram of [(bpy)$_2$Ru(I)Ppd)](PF$_6$)$_2$.H$_2$O
(pH = 4.32 phosphate buffer)
Figure 3-2: $E_{1/2}$ vs pH for $[(bpy)_{2}Ru^{II}(Pptd)](PF_6)_2 \cdot H_2O$
$E_p/2$ vs pH for $[\text{bpy} \text{Ru}^{III}(\text{Ptd})_2](\text{PF}_6)_{2.2}\text{H}_2\text{O}$

Figure 3-27 $E_{1/2}$ vs pH for $[\text{bpy} \text{Ru}^{III}(\text{Ptd})_2](\text{PF}_6)_{2.2}\text{H}_2\text{O}$
Figure 3-28 $E_{1/2}$ vs pH for $[\text{Ru}^{II}(\text{Pptd})_3](\text{PF}_6)_2\cdot 3\text{H}_2\text{O}$