Ruthenium(II) Complexes of a Fused Phenanthroline–Pteridinedione Ligand

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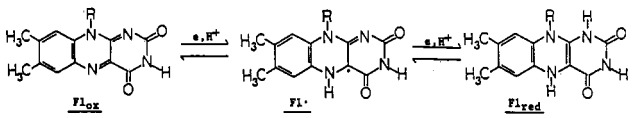
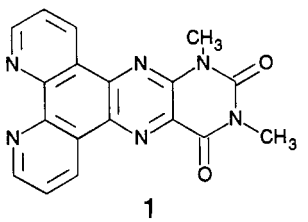
A new alloxazine ligand, produced by the condensation of 1,10-phenanthroline-5,6-dione with 5,6-diamino-1,3-dimethyluracil (**1**; "Pptd") and three ruthenium(II) polypyridyl complexes containing this ligand, $[(bpy)_{3-n}Ru^{II}(Pptd)_n](PF_6)_2 \cdot nH_2O$, have been synthesized. Pptd is a flavin isomer and is thus capable of proton-coupled reductions in aqueous solutions at glassy carbon electrodes. "Clustering" of these Pptd ligands around a Ru(II) center produces stable ruthenium(II) polypyridyl complexes which are in principle capable of being reduced by up to six H atoms (making them potential electrochemical mediators). The synthesis and characterization of the ligand and complexes are discussed. In addition, preliminary data on the pH-dependent reduction (in aqueous solution) of Pptd coordinated to Ru(II) in $[(bpy)_2Ru^{II}(Pptd)]^{2+}$ are presented.

Introduction

Isoalloxazines, or flavins, are tricyclic molecules capable of reversible proton-coupled electron transfer reactions (H-atom transfers). For example, 7,8-dimethyl-benzo[*g*]pteridine-2,4-(3*H*,10*H*)-dione (7,8-dimethylisoalloxazine), shown below, can exist in an oxidized, semi-reduced, or reduced form depending on the pH and the applied potential.[1]



Isoalloxazines are the active sites of the important flavoproteins and are thus responsible for catalyzing many critical biochemical processes.[2] Efforts to take advantage of and even improve upon the H-atom transfer capabilities of these molecules have resulted in numerous synthetically modified isoalloxazines.[3] Coordination of a transition metal can also strongly influence the properties of flavins, but at the cost of blocking at least one of the redox-active sites on the ligand.[4] We have synthesized a flavin *isomer* (an alloxazine derivative, "Pptd"), **1**, capable of coordinating to Ru(II) through a stable bidentate 1,10-phenanthroline linkage.[5]



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Using the well-known synthetic routes[6] for Ru(II)–polypyridyl complexes, several alloxazine ring systems (up to three on monometallic systems and more on multimetallic complexes) can be placed in close proximity around the metal center. Since each alloxazine 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 six or more H-atoms). Expanding on our earlier work,[7] we report here the synthesis and characterization of the new ligand (**1**) and three ruthenium(II) polypyridyl derivatives $[(bpy)_{3-n}Ru^{II}(Pptd)_n](PF_6)_2 \cdot nH_2O$, where bpy = 2,2′-bipyridine, Pptd = **1**, and n = 1, 2, 3. Preliminary studies involving the pH-dependent reduction of coordinated Pptd in aqueous solutions of $[(bpy)_2Ru^{II}(Pptd)]^{2+}$ are also presented.

Experimental Section

Materials. 1,10-Phenanthroline monohydrate (phen), trifluoromethanesulfonic acid (triflic acid), silver trifluoromethanesulfonate (silver triflate, AgTFMS), sodium tetrafluoroborate ($NaBF_4$, 98%), 5,6-diamino-1,3-dimethyluracil hydrate, ammonium hexafluorophosphate (NH_4PF_6, 99.99%), ruthenium trichloride ($RuCl_3 \cdot xH_2O$, 3.8% H_2O) and potassium antimonyl tartrate hydrate ($KSb[C_4H_2O_6] \cdot H_2O$, 99+%) were purchased from Aldrich Chemical Co. and used as received. The disodium salt of ethylenediaminetetraacetic acid ($Na_2EDTA \cdot 2H_2O$) was purchased from Fisher Chemical and used as received. Reagent grade cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) was recrystallized once from hot water. Water for solutions and electrochemical measurements was purified using a Millipore Milli-Q system fed by house-deionized water. Acetonitrile used for electrochemical measurements was purchased either from Burdick & Jackson or Aldrich Chemical Co. (HPLC Grade) and stored over activated molecular sieves (4A). Photometric grade dimethyl sulfoxide was purchased from Aldrich and stored over molecular sieves (3A).

1,10-Phenanthroline-5,6-dione (phen-dione).[8,9] This compound was synthesized by using methods analogous to those reported by Gillard et al.[10] and Szafran.[11] A typical preparation was as follows: $[Co^{II}(phen)_3]$-

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(1) (a) Zubay, G. *Biochemistry*; Wm. C. Brown Publishers: Dubuque, IA, 1993; p 289. (b) Muller, F. In *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer-Verlag: Berlin, Heidelberg, Germany, 1983; Vol. 108, pp 71–107.

(2) (a) Bruice, T. C. *Acc. Chem. Res.* **1980**, *13*, 256. (b) Walsh, C. *Ibid.* **1980**, *13*,148.

(3) (a) Bruice, T. C.; Chan, T. W.; Taulane, J. P.; Yokoe, I.; Elliot, D. L.; Williams, R. F.; Novak, M. *J. Am. Chem. Soc.* **1977**, *99*, 6713. (b) Bruice, T. C.; Chan, R. L. *Ibid.* **1977**, *99*, 6721. (c) Yoneda, F.; Koga, M.; Yano, Y. *J. Chem. Soc., Perkin Trans. I* **1988**, 1813.

(4) (a) Clarke, M. J.; Dowling, M. G. *Inorg. Chem.* **1981**, *20*, 3506. (b) Shinkai, S.; Ishikawa, Y.; Manabe, O. *Chem. Lett.* **1982**, 809. (c) Bessenbacher, C.; Kaim, W. *Z. Anorg. Allg. Chem.* **1989**, *577*, 39. (d) Abelleira, A.; Galang, R. D.; Clarke, M. J. *Inorg. Chem.* **1990**, *29*, 633.

(5) 10,12-Dimethylpteridino[6,7-*f*][1,10]phenanthroline-11,13(10*H*,12H)-dione.

(6) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

(7) We first reported the synthesis and initial characterization of Pptd and $[(bpy)_2Ru^{II}(Pptd)](PF_6)_2$ in 1991: Black, K.; McGuire, M. E. *Abstracts of Papers*, 1991 Joint Central-Great Lakes Regional Meeting of the American Chemical Society, Indianapolis, IN, 1991; INORG 222.

(8) We attempted two *direct* preparations of phen-dione from phen by following methods reported by others.[9a,b] The first method[9a] records a yield of 2.2–3.8%, and a more recent modification[9b] reports 20%. Our yields using these two methods were approximately 1% and 1.75%, respectively. (For the preparation reported in 9b we used 30% oleum instead of 20%.) Other methods for the direct preparation of phen-dione have also been reported.[9c]

(9) (a) Smith, G. F.; Cagle, F. W., Jr. *J. Org. Chem.* **1947**, 781. (b) Amouyal, E.; Homsi, A.; Chambron, J. C.; Sauvage, J. P. *J. Chem. Soc., Dalton Trans.* **1990**, 1841. (c) Conrad, R. C.; Rund, J. V. *Inorg. Chem.* **1972**, *11*, 129.

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$[Sb(C_4H_2O_6)]_2$ (15.94 g, previously prepared by the method of Lee et al.[12]) was added to a stirring solution of 2 mL of bromine in 320 mL of water. After the suspension had been refluxed gently for 1 h, 25 g of $NaBF_4$ was added and the mixture turned a clear dark orange-brown color. The solution was refluxed for an additional 30 min and cooled to room temperature. After cooling in ice, the mixture was filtered and the solid product vacuum-dried. This procedure yielded 10.74 g of dark orange $[Co^{III}(phen)_3](BF_4)_3$.

$[Co^{III}(phen)_3](BF_4)_3$ (5.00 g) was added to 53 mL of concentrated sulfuric acid that had been previously chilled in ice. After addition of 2.63 g of NaBr to the stirring suspension (still under ice), 27 mL of previously chilled concentrated nitric acid was added slowly (in 2-mL portions). The suspension was stirred in ice for 5 min (loosely stoppered[13]) and then gently refluxed for 1 h.[14] After the dark orange-red mixture cooled to room temperature, it was slowly poured into a stirring ice-cooled solution of 16.7 g of NH_4PF_6 in 167 mL of water. The yellow suspension formed was heated very gently without stirring for 30 min and then cooled in an ice bath. The yellow solid obtained after filtration (crude $[Co^{III}(phen\text{-}dione)_3](PF_6)_3$) was air-dried.

Crude phen-dione was isolated by adding $[Co^{III}(phen\text{-}dione)_3](PF_6)_3$ (the entire sample obtained from the above procedure) to a solution of 4.12 g of $Na_2EDTA{\cdot}2H_2O$ dissolved in 167 mL of water. The pH was adjusted to 5.5 with Na_2CO_3, and the mixture was refluxed for 1 h. The mixture was then cooled to room temperature and filtered. The yellow solid obtained after filtering was washed with a few drops of water to remove any residual red-purple stains[15] and then air-dried. The filtrate (also containing phen-dione) and the wash from the solid were combined and extracted several times with 50 mL of chloroform. The combined chloroform extracts were evaporated and combined with the solid collected from the filtration.

The crude phen-dione was refluxed in 108 mL of methanol for about 5 min, and the hot mixture was filtered. Phen-dione usually precipitated immediately out of the filtrate. The filtrate suspension was then reheated to dissolve the product and then slowly cooled to room temperature and then cooled in ice to promote crystallization. The bright yellow crystals were filtered and washed with cold methanol (10 mL) and ether (20 mL) and then vacuum-dried. This procedure[16,17] yielded 1.32 g of pure phen-dione (36% based on $[Co^{III}(phen)_3](BF_4)_3$): mp = 252–257 °C (lit.[9a] mp 256–257 °C).

Pptd. This ligand was synthesized by condensing phen-dione with 5,6-diamino-1,3-dimethyluracil in dry methanol (previously dried over 3A molecular sieves). A typical (optimized) preparation was as follows: Phen-dione (1.36 g, 6.47 mmol) was dissolved in 100 mL of hot methanol and combined with 1.32 g (7.76 mmol) of (vacuum-dried) 5,6-diamino-1,3-dimethyluracil hydrate that had been previously dissolved in 60 mL of hot methanol. An immediate red color quickly gave way to a pea-green suspension during a 1-h reflux. After cooling to room temperature, the suspension was filtered and the solid washed with methanol (2 × 5 mL) and ether (2 × 10 mL) and air-dried. Yield: 1.68 g.

The solid was suspended in 200 mL of chloroform for 30 min and filtered. The light yellow filtrate was combined with a second extraction of the solid (120 mL of chloroform for 10 min). After evaporation, 963 mg (~43% yield) of yellow Pptd ligand was obtained.

The ligand was recrystallized by suspension in 290 mL of a hot solution of absolute ethanol and 0.1 M triflic acid (50:50 v/v). The hot solution was filtered, and the filtrate was slowly cooled to room temperature. The precipitate was filtered, washed with 0.1 M triflic acid (10 mL), water (10 mL), acetone (10 mL), and ether (10 mL), and vacuum-dried.[18] Yield: 771 mg (35% based on phen-dione). Mp: 385–389 °C dec. Anal. Calcd for $C_{18}H_{12}N_6O_2$: C, 62.79; H, 3.51; N, 24.41. Found: C, 62.80; H, 3.51; N, 24.33. IR (KBr): $\nu_{C=O}$ 1676, 1720 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz), ppm (TMS): 3.66 (s, 3H, methyl), 3.98 (s, 3H, methyl), 7.84 (m, 2H), 9.30 (dd, 1H), 9.37 (dd, 1H), 9.43 (dd, 1H), 9.62 (dd, 1H).

$[(bpy)_2Ru^{II}(Pptd)](PF_6)_2{\cdot}H_2O$. $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (0.429 g, 0.824 mmol)[19] and 0.421 g of silver triflate (1.64 mmol) were added to 100 mL of acetone that had previously been deoxygenated with argon for 30 min. The mixture was left to stir under argon for 2 h and then quickly filtered. The Pptd ligand (0.369 g, 1.07 mmol) and 950 mL of previously deoxygenated absolute ethanol were added. After the mixture was refluxed for 1.5 h, 470 mL more deoxygenated absolute ethanol was added[20] and brought to reflux. The mixture was transferred to crystallizing dishes and left to evaporate in a fume hood overnight. The following day, the ~500 mL of solvent remaining was filtered, and the filtrate was evaporated to dryness on a rotary evaporator. The solids obtained were combined, dissolved in 30 mL of acetone, and reprecipitated by dropwise addition to 300 mL of swirling ether. After drying, the 648 mg of crude $[(bpy)_2Ru^{II}(Pptd)](TFMS)_2$ was dissolved in 35 mL of acetone, and then 25 mL of water was added. The mixture was stirred for 15 min and filtered on a fine frit (this removed a small amount of yellow-orange solid), and solid NH_4PF_6 (0.600 g) was added to the stirring filtrate. Slow evaporation of the acetone from the filtrate produced a large amount of orange product which was filtered, washed with cold water (2 mL), cold absolute ethanol (2 mL), chloroform (5 mL), and excess ether. The product was further purified by suspending it in ~40 mL of water at 70 °C and adding acetonitrile (dropwise) until the solid just dissolved. The solution was then cooled very slowly, and the the dark red crystals obtained were filtered, washed with cold water (1 mL), absolute ethanol (1 mL), and ether (~15 mL), and vacuum-dried for 10 h. Yield: 384 mg (44%). Anal. Calcd for $[(bpy)_2Ru^{II}(Pptd)](PF_6)_2{\cdot}H_2O$: C, 42.83; H, 2.84; N, 13.14. Found: C, 42.57; H, 2.94; N, 13.11. IR (KBr): $\nu_{C=O}$ 1682, 1726 cm^{-1}. ^1H NMR (CH_3CN, 300 MHz), ppm (TMS): 3.53 (s, 3H, methyl), 3.91 (s, 3H, methyl), 7.24 (m, 2H), 7.46 (m, 2H), 7.67 (m, 2H), 7.86 (m, 4H), 8.01 (tt, 2H), 8.14 (m, 3H), 8.24 (dd, 1H), 8.53 (t, 4H), 9.47 (dd, 1H), 9.57 (dd, 1H).

$[(bpy)Ru^{II}(Pptd)_2](PF_6)_2{\cdot}2H_2O$. $Ru(bpy)Cl_4$[21] (0.0465 g, 0.116 mmol) and 0.1670 g of Pptd (0.485 mmol) were refluxed in 30 mL of ethylene glycol for 1.75 h. (The color changed from grey-green to brown to red during the reflux.) After the mixture was cooled to room temperature, 30 mL of water was added and the resulting mixture was filtered. Solid NH_4PF_6 was added to the filtrate until precipitation was complete and the mixture was filtered. The solid obtained was washed with 2 mL each of cold water, cold absolute ethanol, and chloroform and then with excess ether.

After vacuum drying, the crude solid was purified using a two-step procedure. First, it was stirred in 20 mL of acetone for 5 min and then filtered. Ether was added dropwise to the stirring filtrate to reprecipitate the complex. The mixture was filtered and the solid washed with ether and vacuum-dried.

The dried solid was then dissolved in just 2.5 mL of acetone and 5 mL of chloroform was added. Ether was added dropwise to this solution until precipitation occurred and the supernatant retained a pale yellow color. The mixture was filtered and the solid washed with 2 mL of chloroform and excess ether and then vacuum-dried for 3.5 h. Yield of dark orange product: 98 mg (65.5%). Anal. Calcd for $[(bpy)Ru^{II}(Pptd)_2](PF_6)_2{\cdot}H_2O$: C, 43.43; H, 2.85; N, 15.42. Found: C, 43.46; H, 2.92; N, 15.46. IR (KBr): $\nu_{C=O}$ 1680, 1725 cm^{-1}.[22] ^1H NMR (CH_3CN, 300 MHz), ppm (TMS): 3.52, 3.53 (s, 6H, methyl), 3.89, 3.91, 3.92 (s, 6H, methyl), 7.32

(10) Gillard, R. D.; Hill, R. E. E.; Maskill, R. *J. Chem. Soc. A* **1970**, 1447.
(11) Szafran, Z.; Pike, R. M.; Singh, M. M. *Microscale Inorganic Chemistry-A Comprehensive Laboratory Experience*; John Wiley & Sons, Inc.: New York, 1991; pp 282–287.
(12) Lee, C. S.; Gorton, E. M.; Neumann, H. M.; Hunt, H. R., Jr. *Inorg. Chem.* **1966**, *5*, 1397.
(13) There appeared to be a fair amount of orange-red vapor produced (Br_2 and NO_2?) which we tried to prevent from escaping the reaction flask without creating a pressure buildup.
(14) *Caution!* We considered this reaction to be potentially explosive. Therefore, 5 g of $[Co^{III}(phen)_3](BF_4)_3$ was the largest amount oxidized in any run, and the reaction was carried out behind a shield. During the reflux, condensation of red liquid more than half way up the reflux column was taken as a sign of overheating.
(15) The red-purple stains are presumably Co–EDTA complexes.
(16) Bruice et al.[17] have reported that phenanthrolinequinones react with both water and methanol. However, they found that the 1,10-phenanthroline-5,6-dione was the *least* reactive.
(17) Eckert, T. S.; Bruice, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 4431.
(18) The elemental analysis and other physical data on this compound were obtained for a sample that had also been dried in a vacuum oven at 120 °C for ~10 h.
(19) (a) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334. (b) Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 4947.
(20) (a) The large amount of absolute ethanol was necessary to dissolve all the Pptd ligand. The preparations of $[(bpy)Ru^{II}(Pptd)_2](PF_6)_2$ and $[Ru^{II}(Pptd)_3](PF_6)_2$ (described in the Experimental Section) were carried out using only 30 mL of refluxing ethylene glycol in a manner similar to that used by Meyer et al.[20b] This method would most likely be useful for $[(bpy)_2Ru^{II}(Pptd)](PF_6)_2$. (b) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, 22, 1617.
(21) (a) Krause, R. A. *Inorg. Chim. Acta* **1977**, *22*, 209. (b) We actually formulate this compound as $Ru^{III}(bpy)Cl_3(H_2O)$ for our syntheses.
(22) The reported frequency at 1680 cm^{-1} is actually the average between "splittings" of equal intensity at the tip of the CO stretch: 1684, 1676 cm^{-1}. The other CO stretch (centered at 1725 cm^{-1}) also showed some evidence of splitting.

(t, 1H), 7.78 (m, 1H), 7.81 (m, 2H), 7.95 (t, 1H), 8.05–8.36 (overlapping multiplets, 4H), 8.56 (d, 1H), 9.41–9.64 (several multiplets, 3H).[23]

$[Ru^{II}(Pptd)_3](PF_6)_2 \cdot 3H_2O$. $RuCl_3 \cdot xH_2O$ (3.8% H_2O; 0.0514 g, 0.238 mmol) and 0.3266 g of Pptd (0.948 mmol) were suspended in 30 mL of ethylene glycol and refluxed for 2 h. Solid NH_4PF_6 (0.39 g) was added, and the mixture was stirred for 5 min and then cooled to room temperature. The solid obtained after filtration was washed with 2 mL each of cold water and cold absolute ethanol, 30 mL of chloroform (in ~5-mL increments), and excess ether.

The vacuum-dried (4 h) crude solid was then dissolved in 25 mL of acetone and filtered. About 20 mL of ether was added dropwise to the stirring dark orange-red filtrate, and the resulting suspension (very light yellow supernatant) was filtered. The solid was washed with cold water (2 mL), absolute ethanol (2 mL), and excess ether and then vacuum dried (4 h).

The solid was then redissolved in 20 mL of acetone, and an equal volume of chloroform was added. This resulted in immediate precipitation of solid product, which was filtered and vacuum-dried for 3 h (169 mg). More solid product was obtained from the filtrate by reprecipitation with ether (leaving a light yellow supernatant). The solid obtained from the filtrate was washed with chloroform (1 mL) and ether (3 mL) and vacuum-dried (57 mg). Both dark orange solids gave essentially identical elemental analyses. Total yield: 226 mg (66%). Anal. Calcd for $[Ru^{II}(Pptd)_3](PF_6)_2 \cdot 3H_2O$: C, 43.88; H, 2.86; N, 17.06. Found: C, 43.81; H, 3.08; N, 16.97. IR (KBr): $\nu_{C=O}$ 1677, 1724 cm^{-1}. ^1H NMR (CH_3CN, 300 MHz), ppm (TMS): 3.53 (s, 9H), 3.91 (s, 9H), 7.80 (m, 6H), 8.24 (overlapping multiplets, 6H), 9.50 (ddd, 3H), 9.59 (dt, 3H).

Methods. Spectral data were obtained in spectrophotometric-grade solvents using a Shimadzu UV-3100 UV–vis–near-IR instrument. FT-IR spectra were taken with a Nicolet 20-DXB instrument. NMR data were obtained with a General Electric QE 300-MHz FT-NMR spectrometer. Electrochemical measurements were carried out using a PAR 173 potentiostat/galvanostat controlled by a PAR 175 universal programmer and recorded on a Houston Instruments 200 XY recorder. Cyclic voltammograms were obtained in a single glass cup (~2-mL samples) using either platinum or glassy-carbon working electrodes (Bioanalytical Systems), a platinum auxiliary electrode, and a saturated sodium chloride calomel (SSCE) reference electrode (Bioanalytical Systems). Elemental analyses were carried out by Atlantic Microlab, Inc.

Results and Discussion

Spectroscopic Measurements. The carbonyl stretching frequencies of Ppdt both increase by 6 cm^{-1} upon coordination to Ru(II) in $[(bpy)_2Ru^{II}(Pptd)](PF_6)_2 \cdot H_2O$. This is consistent with coordination of Pptd to Ru(II) through the 1,10-phenanthroline linkage, remote from the carbonyl sites. An increase in the stretching frequencies of C=O bonds remote from the site of metal coordination has also been observed by Abruna et al[24] for phen-dione in $[(bpy)_2Ru^{II}(phen\text{-}dione)]^{2+}$. Although the resolution of the observed IR spectra (4 cm^{-1}) preclude quantitative comparisons, it is interesting to note that as the number of coordinated Pptd ligands increases from 1 to 3, the C=O stretching frequencies[25] more closely approximate those of the free ligand, which is consistent with "dilution" of the effect of Ru(II) coordination.

UV–vis data for both Pptd and the three Ru(II) complexes are listed in Table I. Chloroform was the only solvent we found in which Pptd was sufficiently soluble (at room temperature) to calculate absorption coefficients.[26,27] When the spectrum of Pptd in acetonitrile is compared to that of 1,10-phenanthroline monohydrate (also in acetonitrile), 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. Thus, the Pptd peaks at 380 nm and 398 nm arise from the pteridinedione portion of the ligand. It is interesting to note that 1,3-dimethyl-2,4(1*H*,3*H*)-pteridinedione (1,3-dimethyllumazine) shows an approximately 25 nm wide envelope of three overlapping absorptions in acetonitrile centered at 331 nm and single strong absorption at 237 nm (see Table I). Thus, the Pptd spectrum can be approximated as the superposition of the 1,10-phenanthroline and pteridinedione peaks, with the 20–25 nm lower energy absorption envelope of pteridinedione being red shifted in the Pptd ligand.

Table I. UV–Vis Data

compound	solvent	λ_{max} (nm) (ϵ (M^{-1} cm^{-1}))[a]
Pptd	$CHCl_3$	402 (1.34 × 10^4)
		383 (1.25 × 10^4)
		273 (sh)
		265 (3.92 × 10^4)
	CH_3CN[b]	398, 380, 264, 239, 217
1,10-phenanthroline hydrate	CH_3CN	275 (sh), 263, 230, 226 (sh), 197
1,3-dimethyllumazine	CH_3CN[c]	237, 324 (sh), 331, 348 (sh)
$[(bpy)_2Ru^{II}(Pptd)](PF_6)_2 \cdot H_2O$	CH_3CN	449 (1.75 × 10^4)
		429 (sh)
		389 (1.86 × 10^4)
		374 (1.84 × 10^4)
		284 (8.40 × 10^4)
		243 (4.97 × 10^4)
		209 (4.92 × 10^4)
$[(bpy)Ru^{II}(Pptd)_2](PF_6)_2 \cdot 2H_2O$	CH_3CN	452 (2.28 × 10^4)
		433 (sh)
		389 (3.63 × 10^4)
		374 (3.49 × 10^4)
		312 (sh)
		279 (1.07 × 10^5)
		242 (7.69 × 10^4)
		207 (6.97 × 10^4)
$[Ru^{II}(Pptd)_3](PF_6)_2 \cdot 3H_2O$	CH_3CN	454 (3.07 × 10^4)
		425 (sh)
		388 (5.37 × 10^4)
		375 (5.13 × 10^4)
		301 (sh)
		278 (1.35 × 10^5)
		242 (1.01 × 10^5)
		208 (8.09 × 10^4)

[a] Absorption coefficients determined with a single concentration. [b] Due to solubility restrictions, absorption coefficients are not reported for Pptd in CH_3CN. [c] Reference 37.

As is typical for hexafluorophosphate salts of Ru(II) polypyridyl complexes, the Ru(II) complexes of Pptd were quite soluble in acetonitrile and acetone and somewhat soluble in water. The spectrum of $[(bpy)_2Ru^{II}(Pptd)](PF_6)_2 \cdot H_2O$ in acetonitrile is shown in Figure 1. Coordination of Pptd to Ru(II) at the 1,10-phenanthroline linkage is confirmed by the presence of the characteristic MLCT absorption band for tris-chelated polypyridyl species around 450 nm and a high-energy shoulder at 429 nm (see also Table I). The maxima assigned as arising from the pteridine-dione portion of Pptd (374, 389 nm) are blue shifted slightly in the metal complexes from the values observed for free Pptd in acetonitrile.

Despite the ease of reduction of coordinated Pptd (~–0.83 V vs SSCE in CH_3CN, vide infra), all three metal complexes remain red or red-orange. It appears that the ligand orbitals involved in the MLCT reduction by Ru(II) (1,10-phenanthroline orbitals) are not strongly coupled to the orbitals involved in the electrochemical reduction (pteridinedione orbitals). A similar observation was made by Ackermann et al.[28] and later by Amouyal et al.[9b] for Ru(II) complexes of dipyrido[3,2-*a*:2′,3′-*c*]phenazine

(23) Despite an excellent elemental analysis, NMR analysis showed that this sample of $[(bpy)Ru^{II}(Pptd)_2](PF_6)_2 \cdot 2H_2O$ was contaminated with what appeared to be *both* $[(bpy)_2Ru^{II}(Pptd)](PF_6)_2 \cdot H_2O$ and $[Ru^{II}(Pptd)_3](PF_6)_2 \cdot 3H_2O$, the latter being the most prevalent contaminant. This caused the NMR integration for $[(bpy)Ru^{II}(Pptd)_2](PF_6)_2 \cdot 2H_2O$ to be less than exact. The original main contamination source was most likely $RuCl_3$ present in the starting material "$Ru(bpy)Cl_4$".

(24) Goss, C. A.; Abruna, H. D. *Inorg. Chem.* **1985**, *24*, 4263.

(25) The C=O stretching frequencies are listed for each compound in the experimental section.

(26) The spectrum in chloroform is limited by the 245-nm UV cutoff.[27]

(27) Sawyer, D. T.; Roberts, J. L. *Experimental Electrochemistry for Chemists*; John Wiley & Sons: New York, 1974; p 183.

(28) Ackermann, M. N.; Interrante, L. V. *Inorg. Chem.* **1984**, *23*, 3904.

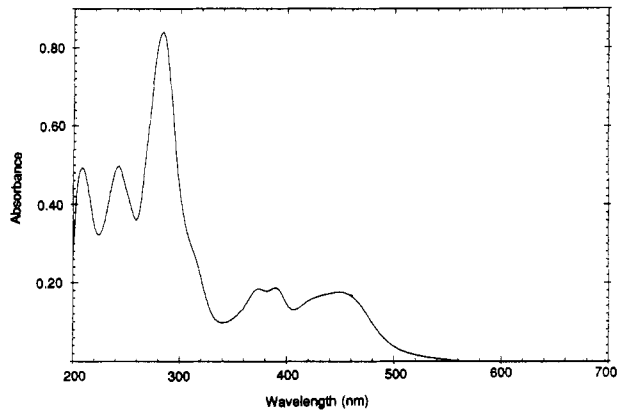

Figure 1. UV–Vis spectrum of 1.00×10^{-5} M $[(bpy)_2Ru^{II}(Pptd)](PF_6)_2 \cdot H_2O$ in CH_3CN.

Table II. Electrochemical Data[a]

compound	solvent[b]	$E_{1/2}$ (V) (ΔE_p (mV))
Pptd	DMSO	–0.84 (130)
$[(bpy)_2Ru^{II}(Pptd)](PF_6)_2 \cdot H_2O$	CH_3CN	+1.34 (75)
		–0.83 (100), –1.40[d]
	DMSO	–0.74 (75), –1.26 (80)
$[(bpy)Ru^{II}(Pptd)_2](PF_6)_2 \cdot 2H_2O$	CH_3CN	+1.39 (75)
	DMSO	–0.78,[c] –0.93,[c] –1.32[d]
$[Ru^{II}(Pptd)_3](PF_6)_2 \cdot 3H_2O$	CH_3CN	+1.42 (80)
	DMSO	–0.72,[d,e] –0.80,[d] –0.93[d]

[a] Pt working electrode, Pt auxiliary electrode, SSCE reference electrode. All solutions purged with N_2 prior to use. $E_{1/2} = (E_c + E_a)/2$; $\Delta E_p = E_c - E_a$ (in mV); E_c and E_a = peak potentials for reduction and oxidation, respectively. [b] Electrolyte: 0.1 M tetrabutylammonium hexafluorophosphate (TBAH). [c] E_c values only. [d] Irreversible reduction. [e] 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.

(dppz). More recently, Kaim et al[29] have reported similar results using a rigorous spectroscopic and electrochemical study of $[(bpy)_2Ru^{II}(dppz)]^{2+}$ combined with a HMO/McLachlan perturbation calculation of π spin populations and orbital energies of the dppz ligand. Their results, which should be applicable to the structurally related Pptd ligand, indicate that the LUMO of dppz is centered in the phenazine portion of the structure, remote from the α-diamine portion of the ligand. The HMO calculations indicated that the MLCT transition from Ru(II) to this LUMO would show a small oscillator strength and would thus be overshadowed by the intense MLCT transition to the (higher energy) "bpy-centered" π^* orbitals. Our observations for Pptd bound to Ru(II) are consistent with their analysis.

Electrochemistry. The results of cyclic voltammetry experiments in both acetonitrile and dimethylsulfoxide are summarized in Table II. In dimethyl sulfoxide, the $E_{1/2}$ of Pptd is estimated to be –0.84 V vs SSCE. As can be observed from Figure 2, a large peak separation, enhanced reduction wave, and a broad anodic wave on the return sweep were observed and are probably due to comparatively slow electrode kinetics and complications from adsorption.

The cyclic voltammogram for $[(bpy)_2Ru^{II}(Pptd)](PF_6)_2 \cdot H_2O$ in acetonitrile is shown in Figure 3. In acetonitrile, all three metal complexes exhibited fairly reversible (ΔE_p = 74–80 mV) oxidations typical of the one-electron metal-centered oxidations of Ru(II) polypyridyl species.[6] It should be noted (Table II) that the $E_{1/2}$ values for the metal-centered oxidations increase monotonically with the number of Pptd ligands. This data and the small shifts in the MLCT transitions and Pptd C=O stretching frequencies, indicate that electronic isolation of the pteridinedione orbitals from Ru(II), while severe, is not total.

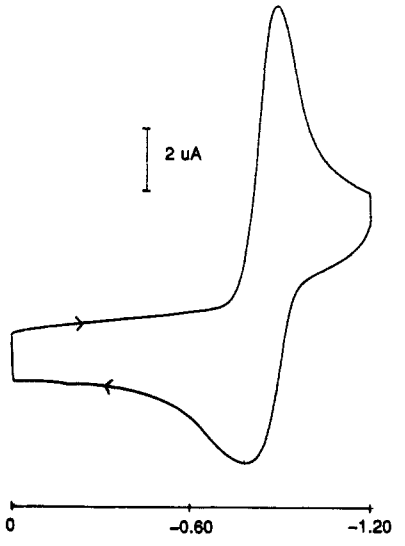

Figure 2. Cyclic voltammogram of Pptd at a Pt electrode in DMSO/0.1 M TBAH at a scan rate of 100 mV/s. Further scans out to –1.8 V produced no new waves.

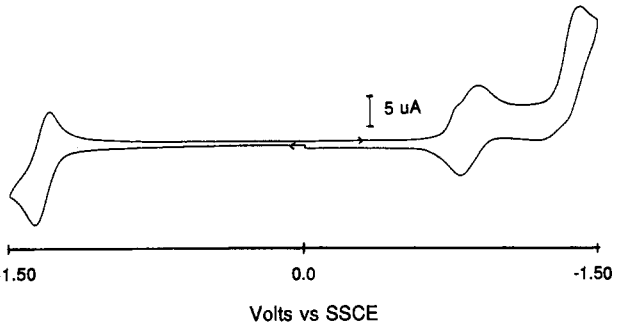

Figure 3. Cyclic voltammogram of $[(bpy)_2Ru^{II}(Pptd)](PF_6)_2 \cdot H_2O$ at a Pt electrode in CH_3CN containing 0.1 M TBAH at a scan rate of 100 mV/s.

Figure 3 also reveals two ligand-based reductions which we have assigned as arising from the pteridine-dione portion of Pptd ($E_{1/2}$ = ~0.83 V) and one of the bipyridines (E_c = ~ –1.4 V). This assignment is consistent with that previously reported for $[(bpy)_2Ru^{II}(dppz)]^{2+}$ in dry DMF.[29] The reduction wave for coordinated Pptd in $[(bpy)_2Ru^{II}(Pptd)]^{2+}$ contains what is presumably an adsorption prewave (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.[30] We assign the Pptd and bipyridine reduction waves as each representing one-electron processes based on a comparison of their relative peak areas with the one-electron metal-centered oxidation at +1.34 V in acetonitrile.

Ligand-based reductions for all three metal complexes appeared to be somewhat more well-behaved in dimethyl sulfoxide. Parts A–C of Figure 4 show reductive scans of the complexes with one, two, and three Pptd ligands, respectively. Both $[(bpy)_2Ru^{II}(Pptd)]^{2+}$ and $[(bpy)Ru^{II}(Pptd)_2]^{2+}$ show a reductive wave at ~ –1.3 V which we have 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 –0.73 to –0.95 V for the complexes with one, two, and three Pptd ligands, respectively. Except for $[(bpy)_2Ru^{II}(Pptd)]^{2+}$ (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 dimethyl sulfoxide.

(29) Fees, J.; Kaim, W.; Moscherosch, M.; Matheis, W.; Klima, J.; Krejcik, M.; Zalis, S. *Inorg. Chem.* **1993**, *32*, 166.

(30) All three Ru(II)–Pptd complexes showed a great tendency to adsorb on electrode surfaces.

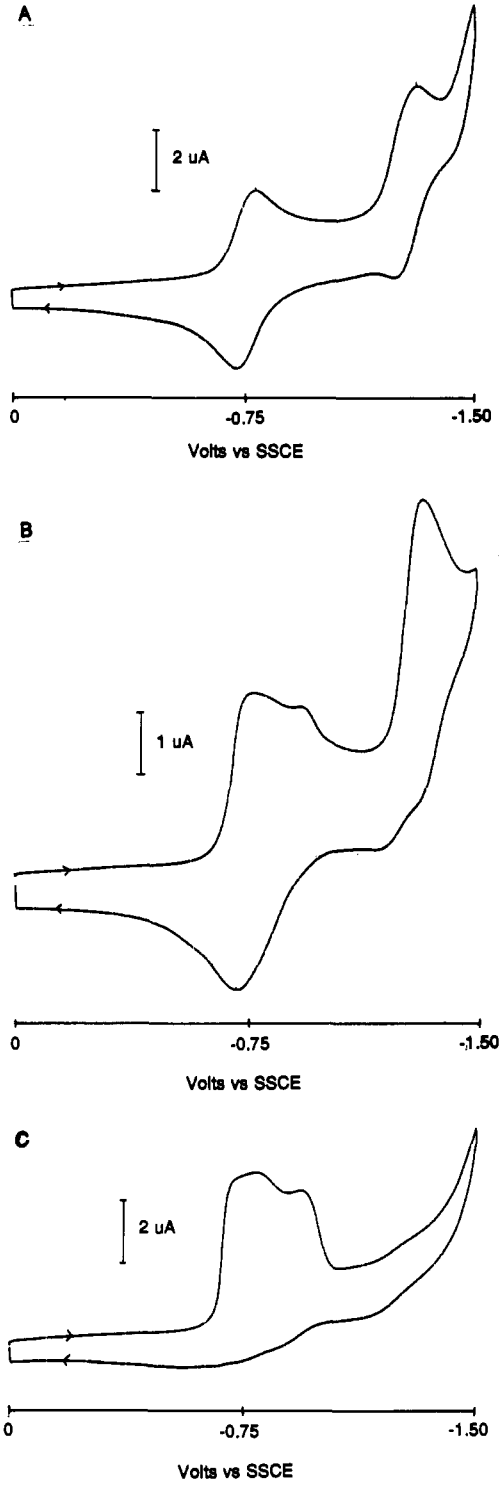

Figure 4. Cyclic voltammograms of (A) $[(bpy)_2Ru^{II}(Pptd)](PF_6)_2 \cdot H_2O$, (B) $[(bpy)Ru^{II}(Pptd)_2](PF_6)_2 \cdot 2H_2O$, and (C) $[Ru^{II}(Pptd)_3](PF_6)_2 \cdot 3H_2O$ each at a Pt electrode in DMSO containing 0.1 M TBAH at a scan rate of 100 mV/s.

Aqueous Electrochemistry of $[(bpy)_2Ru^{II}(Pptd)]^{2+}$. The ability of coordinated Pptd ligands to act as H-atom transfer mediators in solution depends on their tendency to undergo facile proton-coupled reductions at electrode surfaces. We have initiated electrochemical studies in aqueous solutions[31] and will present here preliminary data on the pH-dependent reduction of Pptd in $[(bpy)_2Ru^{II}(Pptd)]^{2+}$.

Figure 5 shows the cyclic voltammogram of $[(bpy)_2Ru^{II}(Pptd)]^{2+}$ in pH = 4.32 phosphate buffer. The metal-centered

(31) Coordination of Pptd to Ru(II) vastly improves the solubility of the ligand in aqueous solutions for all three complexes studied.

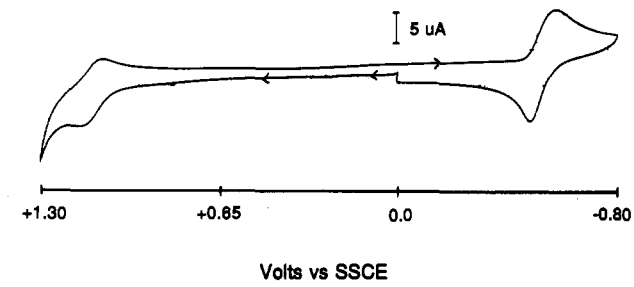

Figure 5. Cyclic voltammogram of $[(bpy)_2Ru^{II}(Pptd)](PF_6)_2 \cdot H_2O$ at a glassy carbon (GC) electrode in 0.10 M NaH_2PO_4 aqueous buffer (pH = 4.32) at a scan rate of 100 mV/s.

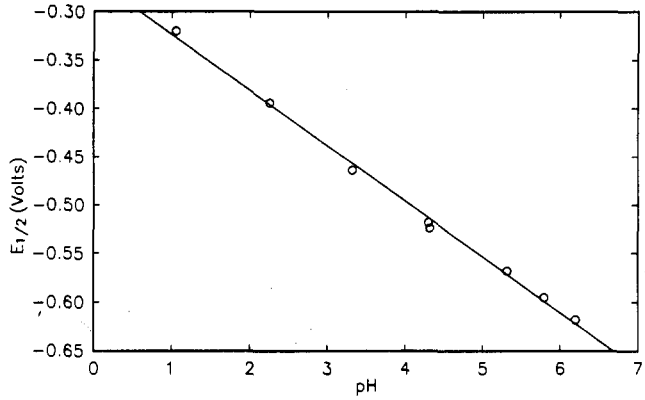

Figure 6. $E_{1/2}$ vs pH diagram for $[(bpy)_2Ru^{II}(Pptd)](PF_6)_2 \cdot H_2O$ using various aqueous buffer solutions. Reported $E_{1/2}$ values are for scans at a GC electrode at a scan rate of 100 mV/s.

oxidation ($E_{1/2}$ = +1.11 V, ΔE_p = 70 mV)) and the Pptd-centered reduction ($E_{1/2}$ = –0.52 V, ΔE_p = 100 mV) are both easier to accomplish in aqueous solution than in acetonitrile. Presumably the shift in the metal-centered oxidation potential is due merely to the higher dielectric constant of water, while the shift in reduction potential is due to the ready availability of hydrogen ions in the buffer. In addition, it would seem reasonable to assume that the ready availability of hydrogen ions could make the reduction of Pptd in aqueous solutions a multielectron process ($2e^-/2H^+$). A comparison of the relative peak areas for Pptd reduction and the one-electron Ru(III/II) couple in Figure 5 is consistent with this assumption. In addition, polarographic and voltammetric studies on pteridine derivatives[32] have shown that, in aqueous solution, the initial reduction step is a reversible $2e^-/2H^+$ process in which reduction takes place across the pyrazine nitrogens.

Figure 6 shows the $E_{1/2}$ vs pH diagram for reduction of Pptd coordinated to $[(bpy)_2Ru^{II}(Pptd)]^{2+}$ in aqueous buffer solutions. A linear-least-squares fit of the data from pH = 1.05 to 6.20 gave a line of slope –57.4 (±1.4)[33] mV/pH which is very close to the theoretical value of –59.5 mV/pH for a $1e^-/1H^+$ or $2e^-/2H^+$ process. On the basis of the known multielectron behavior of both pteridines[32,34] and flavins[1] and the information presented in Figures 5 and 6, we tentatively assign the reduction of coordinated Pptd in $[(bpy)_2Ru^{II}(Pptd)]^{2+}$ as a $2e^-/2H^+$ process.

$$[(bpy)_2Ru^{II}(Pptd)]^{2+} + 2e^- + 2H^+ \rightarrow [(bpy)_2Ru^{II}(PptdH_2)]^{2+}$$

Detailed voltammetric and coulometric studies are now underway

(32) (a) Kwee, S.; Lund, H. *Biochem. Biophys. Acta.* **1973**, *297*, 285. (b) Lund, H. In *Chemistry and Biology of Pteridines*; Pfleiderer, W., Ed.; Walter de Gruyter: Berlin, 1975; pp 645–670. (c) Pfleiderer, W. In *Folates and Pterins*; Blakley, R. L., Benkovic, S. J., Eds.; John Wiley and Sons: New York, 1984; pp 43–114.

(33) Uncertaintly recorded at the 67% confidence level; r^2 = 0.996. Fits calculated using *Axum* by Trimetrix, Inc.

(34) Dryhurst, G. *Electrochemistry of Biological Molecules*; Academic Press: New York, 1977; pp 320–362.

in order to more precisely determine the nature of the reduction of coordinated Pptd in both aqueous and nonaqueous environments for all three Ru(II) complexes.[35]

Conclusions. A pteridinedione has been fused to a 1,10-phenanthroline to form the Pptd ligand which, when 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 ruthenium(II) polypyridyl complexes. We have presented preliminary pH-dependent voltammetric data for $[(bpy)_2Ru^{II}(Pptd)]^{2+}$, and detailed coulometric and voltammetric studies for this and the other complexes are now under way.

Future work will revolve around the modification of the coordinated Pptd ligand in order to facilitate its ability to mediate H-atom tranfers such as the reduction of CO_2 to CO and H_2O.[36] Construction of other stable metal complexes (Fe^{2+}, Co^{3+}) using Pptd (and analogs) is now in progress. In addition, the effect of intentionally modifying electrodes with complexes such as $[(bpy)_2Ru^{II}(Pptd)]^{2+}$, (using Nafion, for example) will also be investigated.

Acknowledgment. Support from the Research Corp. through a Cottrell College Science Grant is gratefully acknowledged. The 300-MHz FT-NMR was obtained through a grant from the National Science Foundation (CHE-8851619) and matching funds from Eastern Illinois University. Helpful discussions in the initial stages of this work with Dr. Dinesh Gala of The Schering-Plough Research Institute are also gratefully acknowledged.

Supplementary Material Available: FT-NMR spectra (300 MHz) of the Pptd ligand (CD_3Cl) and the three metal complexes (CD_3CN) (4 pages). Ordering information is given on any current masthead page.

(35) To be submitted for publication.

(36) (a) For example, the reduction potential of coordinated Pptd seems to fall just short of the reported potential for reduction of CO_2. (–0.56 V for coordinated Pptd at pH = 5.00 vs –0.65 V for CO_2/CO).[36b] (b) Randin, J. P. In *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Ed.; Marcel Decker: New York, 1976; Vol. VIII, p 172.

(37) Juriga, G.; Sattgast, M.; McGuire, M. E. *Inorg. Chim. Acta.* **1991**, *183*, 39.