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Synthesis and characterization of $[(bpy)_2Ru^{II}(1,3\text{-}Me_2Lumazine)](PF_6)_2$

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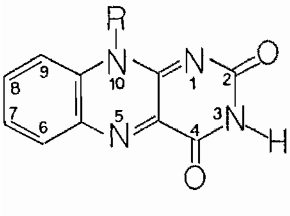
Abstract

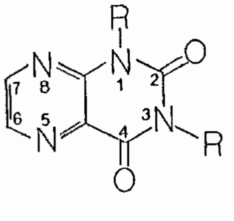
The complex $[(bpy)_2Ru^{II}(1,3\text{-}Me_2Lum)](PF_6)_2$ (where bpy = 2,2′-bipyridine and $1,3\text{-}Me_2Lum$ = 1,3-dimethyllumazine) has been prepared. Infrared and elemental analyses show that Ru(II) binds $1,3\text{-}Me_2Lum$ through the N-5 and O-4 positions on the ligand. Cyclic voltammetry in CH_3CN reveals a nearly reversible wave ($\Delta E_p = 70$ mV) for the complex centered at $E_{1/2} = +1.33$ V (*versus* SSCE). The reduction potential (in CH_3CN) for the coordinated $1,3\text{-}Me_2Lum$ is shifted by +0.800 V relative to that of the free ligand. In water, the complex showed pH-independent (pH = 4.26–9.12) irreversible oxidative waves at ~ +1.2 V. Reductive scans in water gave results that were qualitatively similar to those obtained in CH_3CN. UV–Vis analysis in CH_3CN showed bpy ($\pi \rightarrow \pi^*$) bands at 242 and 285 nm, $1,3\text{-}Me_2Lum$ absorptions around 350–365 nm, and fairly intense MLCT bands centered at 431 and 509 nm.

Introduction

We have recently initiated studies involving the attachment of polypyridyl derivatives of redox active and pH-sensitive flavins (I) and pteridines (II) to Ru(II) complexes. Both flavins and pteridines can undergo proton-coupled electron transfer reactions.



I



II

Their reduced forms may serve as potent H-atom donors. Our long range goal is to anchor one or more of these flavin or pteridine derivatives to stable Ru(II) polypyridyl complexes in such a way as to leave their redox active positions (*i.e.* N1, N5, O4 on flavin) open for interaction with suitable substrates. These complexes could then be used as stable, reusable catalysts capable of multiple H-atom donation.

Clarke *et al.* have reported the *direct* binding of $(NH_3)_4Ru^{II}$ moieties to the N5 and O4 positions of several flavins [1] and pteridines [2]. As a prelude to our studies, we investigated the direct binding of $(bpy)_2Ru^{II}$ fragments to both flavins and pteridines. The attempted synthesis of the complex $[(bpy)_2Ru^{II}(\text{flavin})]^{2+}$ (where flavin = 10-methyl-isoalloxazine) resulted in a low yield of product which was difficult to characterize [3]. This was probably due to steric hindrance from the interaction of the bipyridine rings and the benzo portion of the flavin. The smaller pteridine system, on the other hand, forms stable, robust complexes with the $(bpy)_2Ru^{II}$ moiety. This report deals with the spectroscopic and electrochemical behavior of the Ru(II) polypyridyl complex $[(bpy)_2Ru^{II}(1,3\text{-}Me_2Lumazine)]^{2+}$ (bpy = 2,2′-bipyridine) in which the pteridine derivative 1,3-dimethyllumazine ($1,3\text{-}Me_2Lum$) is *directly* bonded to the Ru(II) center through the N-5 and O-4 sites on the ligand.

Experimental

Materials

Water was deionized using a Millipore Milli-Q^{TM} Water System. Spectral grade acetonitrile (Kodak) was used for UV–Vis measurements, and HPLC grade acetonitrile (Fisher, dried over 3A molecular sieves) and polarographic grade tetraethylammonium perchlorate, TEAP (G. F. Smith), were used for the electrochemical

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measurements. Buffer solutions ($\mu = 0.1$ M) for electrochemical measurements were as follows: pH = 1.0 ($HClO_4$ or HCl), pH = 4.26 and 7.38 (phosphate), pH = 9.12 (borate/Na_2SO_4). Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Synthesis

1,3-Me_2Lum [4] and *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) dihydrate, Ru(bpy)$_2$Cl$_2$ · 2H_2O [5], were prepared by literature procedures. The synthesis of the title compound was carried out in the following manner: 0.1001 g of Ru(bpy)$_2$Cl$_2$ · 2H_2O (1.92×10^{-4} mol) and 0.096 g of silver trifluoromethanesulfonate (Aldrich) (3.7×10^{-4} mol) were dissolved in 100 ml of acetone that had been previously deoxygenated with nitrogen. The mixture was stirred for 3 h under nitrogen, then filtered quickly to remove precipitated silver chloride. The red filtrate was put back under nitrogen in a round bottom flask as soon as possible to avoid air oxidation of the Ru(bpy)$_2$(solvent)$_2{}^{2+}$ species. To the stirring solution was added 0.076 g of 1,3-Me_2Lum (4.0×10^{-4} mol) that had been previously dissolved in 25 ml of acetone (deoxygenated with argon). After 2 h of gentle reflux (under nitrogen), 10 ml of water was added. After 1.5 h of further heating, the reflux column was removed to allow the acetone to evaporate. The remaining water solution was cooled to room temperature, and the product was precipitated by the dropwise addition of a saturated solution of NH_4PF_6 (Aldrich), cooling in ice, and filtering. The precipitate was washed with several drops of cold water, but this did cause the apparent loss of some product.

After drying under vacuum, the crude product (138 mg) was dissolved in 4 ml of warm acetone, followed by the addition of 10 ml of ethanol/water (1:1 vol./vol.). The acetone was then evaporated on a hot plate, and the resulting solution was cooled to room temperature, refrigerated for 1 h, and subsequently stored in the freezer overnight. The precipitated product was filtered and washed with a few drops of cold ethanol (some product lost in washing). Yield: 111 mg (64%). *Anal.* Calc. for $C_{28}H_{24}N_8O_2P_2F_{12}Ru$: C, 37.55; H, 2.70; N, 12.51. Found: C, 36.81; H, 2.66; N, 12.21%.

Instrumentation

UV–Vis measurements were taken on a Shimadzu U-3100 spectrophotometer. IR spectra were recorded in KBr using a Nicolet 20 DXB FT-IR spectrometer. Electrochemical measurements were done using a EG&G PAR model 173 potentiostat/galvanostat controlled by a PAR 175 universal programmer. The working electrodes were either platinum or glassy carbon (BAS: Bioanalytical Systems, Inc.), and the reference was a BAS saturated sodium chloride calomel electrode (SSCE). A platinum wire was used as the auxiliary electrode.

Results and discussion

Evidence for the binding of the [(bpy)$_2$Ru^{II}-]$^{2+}$ fragment to 1,3-Me_2Lum through the N5 and O4 positions on the pteridine ring can be found in the IR analysis. 1,3-Me_2Lum shows two strong carbonyl absorption bands (KBr) at 1661 and 1715 cm^{-1}. In [(bpy)$_2$Ru^{II}(1,3-Me_2Lum)](PF$_6$)$_2$, these stretches appear at 1624 and 1723 cm^{-1}, consistent with coordination of Ru^{II} directly to one carbonyl (presumably O4), and remote from the other (O2). Similar assignments and shifts in the IR spectra of neutral lumazines coordinated to transition metal centers through N5 and O4 were noted by Clarke *et al.* [2] (for Ru(II)) and by Goodgame and Schmidt [6] for Mn(II), Co(II), Ni(II) and Cu(II). It is interesting to note that the increase in stretching frequency of the C=O bond remote from the site of metal coordination is also observed in other transition metal complexes such as [(bpy)$_2$Ru^{II}(phen-5,6-dione)]$^{2+}$, where phen-5,6-dione = 1,10-phenanthroline-5,6-dione [7]. Also, Cook and Regnier reported an increase in stretching frequency of both C=O groups in 1,3,7-trimethylxanthine (structurally similar to 1,3-Me_2Lum) upon protonation at a remote N [8]. On the basis of an acceptable elemental analysis and comparison of the IR data with the literature, we conclude that a single 1,3-Me_3Lum coordinates to [(bpy)$_2$Ru^{II}-]$^{2+}$ through the O4 and N5 positions on the rings.

Figure 1 shows a cyclic voltammogram of [(bpy)$_2$Ru^{II}(1,3-Me_2Lum)]$^{2+}$ in CH_3CN. The complex shows a single, nearly reversible (ΔE_p =

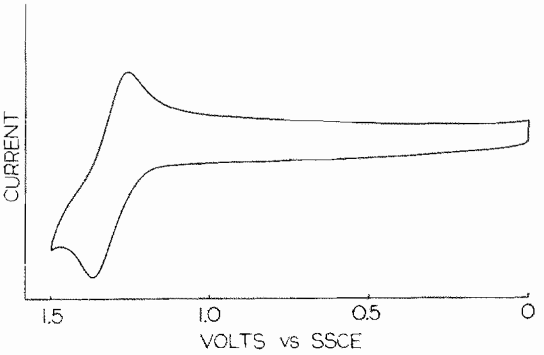

Fig. 1. Cyclic voltammogram (0.0 to +1.5 V) of [(bpy)$_2$Ru^{II}(1,3-Me_2Lum)](PF$_6$)$_2$ in CH_3CN/0.1 M TEAP using a Pt electrode.

70 mV) wave at +1.33 V (*versus* SSCE). The free ligand 1,3-Me_2Lum shows no oxidative waves in CH_3CN out to +1.5 V. The $E_{1/2}$ of +1.33 V for the complex is in the region expected for metal-centered oxidations of $[(bpy)_2Ru^{II}(LL)]^{2+}$ compounds where LL = an electron deficient heterocyclic ring [9]. The complex $[(bpy)_2Ru^{II}$(2-CHOpy)]$(PF_6)_2$ (where 2-CHOpy = 2-pyridinecarboxaldehyde), recently prepared by Goldsby and Blaho [10], shows an *irreversible* wave in CH_3CN at ~+1.3 V (*versus* SSCE), which is quite close to the $E_{1/2}$ value we observe for $[(bpy)_2Ru^{II}$(1,3-Me_2Lum)]$(PF_6)_2$.

Reductive scans in CH_3CN produce an irreversible wave at ~−0.69 V, followed by what appear to be two consecutive reductions ($E_{1/2}$ values estimated at −1.52 and −1.76 V, respectively) near the solvent limit in our system (Fig. 2). In CH_3CN, the free ligand 1,3-Me_2Lum shows an irreversible reduction at −1.47 V. On the basis of comparison with the well-known $[Ru^{II}(bpy)_3]^{2+}$ complex, the waves at −1.52 and −1.76 V most likely represent one electron reductions of each bpy ligand [11]. Apparently then, in CH_3CN, the coordinated 1,3-Me_2Lum is reduced at the electrode surface at ~−0.69 V, which is about 0.800 V positive of the cathodic wave observed for the free ligand.

Oxidative scans of $[(bpy)_2Ru^{II}$(1,3-Me_2 Lum)$]^{2+}$ in water at pH = 4.26, 7.38 and 9.10 produced irreversible and pH-independent anodic waves at −1.2 V. The complex $[(NH_3)_4Ru^{II}$(1,3-Me_2Lum)]Br_2, on the other hand, has been reported to show a reversible wave at around 0.66 V (*versus* Ag/AgCl) [2] at similar pHs. The fact that our complex is harder to oxidize is not surprising, since, for example, $E_{1/2}[Ru(bpy)_3]^{3+/2+} - E_{1/2}$ $[(NH_3)_4Ru(bpy)]^{3+/2+}$ = 0.78 V (in CH_3CN) [12]. Destabilization of $[(bpy)_2Ru^{III}$(1,3-Me_2Lum)$]^{3+}$ relative to the tetraammine analog is probably due in part to the competition between the 1,3-Me_2Lum and the bpy ligands for π-backbonding electron density. In water, the complex $[(bpy)_2$-Ru^{II}(2-CHOpy)]$(PF_6)_2$ shows reversible oxidative electrochemistry, but it is accompanied by reversible hydrolysis on the 2-CHOpy ligand [10]. This type of reversible chemistry is apparently not available to the $[(bpy)_2Ru^{II}$(1,3-Me_2Lum)]$(PF_6)_2$ complex, at least on the CV time scale.

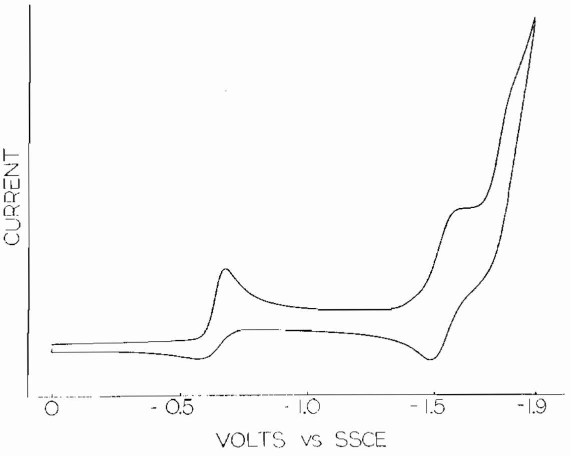

Fig. 2. Cyclic voltammogram (0.0 to −1.9 V) of $[(bpy)_2Ru^{II}$(1,3-Me_2Lum)]$(PF_6)_2$ in CH_3CN/0.1 M TEAP using a Pt electrode. Scans out to only −0.9 V did not significantly enhance the reversibility of the reduction of the coordinated 1,3-Me_2Lum.

Reductive scans in water at pH = 1.00, 4.26, 7.38 and 9.10 of both free and coordinated 1,3-Me_2Lum produce somewhat complex voltammograms. However, the key features are similar to those obtained in CH_3CN. For $[(bpy)_2Ru^{II}$ (1,3-Me_2Lum)]$(PF_6)_2$ irreversible and pH-independent (at least from pH = 4.26 to 9.10) reductions are observed that are 300–500 mV more positive than those obtained for the free ligand. Electrochemical data in both CH_3CN and H_2O are summarized in Table 1.

The UV–Vis spectra of $[(bpy)_2Ru^{II}$(1,3-Me_2Lum)]$(PF_6)_6$ in CH_3CN is shown in Fig. 3. The usual bpy($\pi \rightarrow \pi^*$) bands at 285 and 242 nm are present in the spectrum [9]. The Ru^{II} complex also shows broad absorption bands at 431 and 509 nm, which are consistent with $Ru^{II} \rightarrow$ ligand MLCT transitions out on to the bipyridines and the more electron deficient 1,3-Me_2Lum ligand, respectively [11]. In addition, the Ru^{II} complex exhibits a broad and not well defined absorption at around 350–365 nm, which may be attributed to ligand centered transitions in the 1,3-Me_2Lum which are red shifted upon coordination to $[(bpy)_2Ru^{II} -]^{2+}$. (Free 1,3-Me_2Lum shows absorption peaks at 237 and 331 nm, with the 331 nm peak having shoulders at ~324 and 348 nm and an absorption coefficient close to that observed for the lumazine peaks in the complex.)

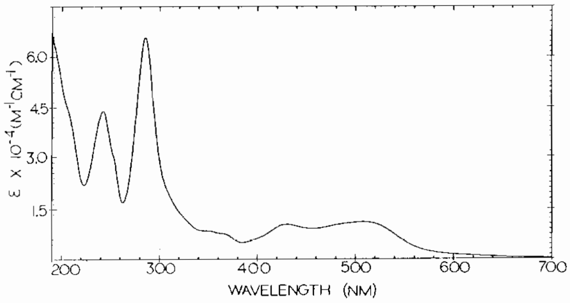

Fig. 3. UV–Vis spectra of $[(bpy)_2Ru^{II}$(1,3-Me_2Lum)]$(PF_6)_2$ in CH_3CN.

TABLE 1 Summary of cyclic voltammetry data[a]

Solution	$[(bpy)_2Ru^{II}(1,3\text{-}Me_2Lum)](PF_6)_2$	1 3-Me_2Lum
CH_3CN/0 1 M TEAP	+1 33 (70) −0 69 (irr) −1 52 (111) −1 76[b]	−1 47 (irr)
pH = 1 00 (0 1 M HCl)	−0 55 (irr)[c]	
pH = 1 00 (0 1 M $HClO_4$)		−0 34 (irr)[d]
pH = 4 26 (phosphate)	+1 20 (irr)[e] −0 74 (irr)[f]	−1 20 (irr)[d g]
pH = 7 38 (phosphate)	+1 20 (irr)[h] −0 74 (irr)[i]	−1 02 (cath) −0 60 (anod)
pH = 9 12 (borate/Na_2SO_4)	+1 20 (irr) −0 75 (irr) −1 19 (irr)	−1 06 (cath) −0 66 (anod)

[a]Platinum (for CH_3CN) or freshly polished glassy carbon (for aqueous solutions) working electrodes were used, along with a Pt auxiliary electrode, and a saturated sodium chloride calomel (SSCE) reference electrode Potentials are in volts Values in brackets indicate peak separations ($\Delta E_p = E_{anodic} - E_{cathodic}$) in mV Where actual peak separations are not given, values are *actual* peak positions, *not* estimated $E_{1/2}$ values (unless otherwise noted) [b]Estimated $E_{1/2}$ (very close to solvent/electrolyte limit) [c]An additional small cathodic wave was observed at ~ −0 82 V An oxidative wave was not observed before the solvent/electrolyte limit [d]Consecutive scans caused a sharp decrease in peak current [e]After scanning to +1 4 V, waves at +0 94 V and ~ +0 52 V appeared on the reverse scan [f]An additonal small cathodic wave was observed at ~ −0 90 V [g]After the first scan, a small cathodic wave appeared at ~ −0 88 V [h]After scanning to +1 5 V, waves at +0 63 and ~ +0 36 V appeared on the reverse scan [i]A small additional peak appeared at −0 56 V

From our results it seems evident that, at least in water, neither free 1,3-Me_2Lum nor its coordinated form in $[(bpy)_2Ru^{II}(1,3\text{-}MeLum)](PF_6)_2$ appear to be ideal candidates for reversible redox chemistry This was not surprising, given the complex electrochemical behavior of substituted pteridines noted in the literature [13] However, we were surprised at the robust nature (and oxidative stability) of the complex in CH_3CN, and investigations of other polypyridyl Ru(II) pteridine complexes in both aqueous and non-aqueous media are now in progress

Acknowledgements

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References

1 (a) M J Clarke, M G Dowling, A R Garafalo and T F Brennan, *J Biol Chem*, *255* (1980) 3472, (b) M G Dowling and M J Clarke, *Inorg Chim Acta*, *78* (1983) 153, (c) M J Clarke, *Rev Inorg Chem*, *II*, (1980) 28
2 A Abelleira, R D Galang and M J Clarke, *Inorg Chem*, *29* (1990) 633
3 M E McGuire and R A Pavinato, *Abstr of Papers, 198th National Meet American Chemical Society, Miami Beach, FL*, American Chemical Society, Washington, DC, 1989, INORG 385
4 H I X Mager and W Berends, *Recl Trav Chim Pays-Bas*, *91* (1972) 1137
5 (a) B P Sullivan, D J Salmon and T J Meyer, *Inorg Chem*, *17* (1978) 3334, (b) G Sprintschnik, H W Sprintschnik, P P Kirsch and D G Whitten, *J Am Chem Soc*, *99* (1977) 4947
6 M Goodgame and M A Schmidt, *Inorg Chim Acta*, *36* (1979) 151
7 C A Goss and H D Abruna, *Inorg Chem*, *24* (1985) 4263
8 D Cook and Z R Regnier, *Can J Chem*, *45* (1967) 2895
9 R Sahai, L Morgan and D P Rillema, *Inorg Chem*, *27* (1988) 3495
10 K A Goldsby and J K Blaho, *J Am Chem Soc*, *112* (1990) 6132
11 D P Rillema, G Allen, T J Meyer and D Conrad, *Inorg Chem*, *22* (1983) 1617
12 J C Curtis, B P Sullivan and T J Meyer, *Inorg Chem*, *22* (1983) 224
13 (a) A Kwee and H Lund, *Biochim Biophys Acta*, *297* (1973) 285, (b) G Dryhurst, *Electrochemistry of Biological Molecules*, Academic Press, New York, 1977, pp 320–362, (c) J Lehnen, B M White and M J Kendrick, *Inorg Chim Acta*, *167* (1990) 257