



Review

Electronic structures, photophysical properties, and electrochemistry of ruthenium(II)(bpy)₂ pyridylimidazole complexesKyle M. Lancaster^a, James B. Gerken^b, Alec C. Durrell^a, Joshua H. Palmer^a, Harry B. Gray^{a,*}^a Beckman Institute, California Institute of Technology, 1200 E California Blvd, Pasadena, CA 91125, USA^b Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706, USA

Contents

1. Introduction	1803
2. Properties of Ru ^{II} complexes with pyridylimidazole and related ligands	1804
3. Absorption spectra	1805
4. Redox properties	1805
5. Excited state properties	1806
6. Acid–base behavior	1806
7. Theory	1807
8. Conclusions	1809
9. Syntheses	1809
10. Spectroscopic methods	1810
11. Electrochemical methods	1810
12. Computational methods	1810
Acknowledgements	1810
References	1810

ARTICLE INFO

Article history:

Received 20 August 2009

Accepted 9 April 2010

Available online 24 April 2010

Keywords:

Ruthenium
Pyridylimidazoles
Photophysics
Cyclic voltammetry

ABSTRACT

The properties of Ru^{II} complexes involving the imidazole moiety are discussed. Complexes [Ru(bpy)₂(L)]²⁺ [bpy = 2,2'-bipyridine, L = 2-(2'-pyridyl)imidazole (2-pimH) and 4-(2'-pyridyl)imidazole (4-pimH)] have been synthesized and fully characterized. Reduction potentials are 0.76 V vs. Fc⁺/Fc⁰ for both complexes in acetonitrile solution, and the deprotonated complexes undergo irreversible electrochemical oxidation at 0.38 V vs. Fc⁺/Fc⁰. Density functional theory (DFT) calculations suggest that oxidation of the protonated complexes is primarily metal-based and that of the deprotonated complexes is ligand-centered. The pK_a of the 4-pimH complex was found to be 9.7 ± 0.2; the pK_a of the 2-pimH complex is 7.9 ± 0.2. Luminescence lifetimes (L = 4-pimH, 277 ns; 2-pimH, 224 ns; 4pim⁻, 40 ns; 2pim⁻, 34 ns in 5% methanol/water solution) combined with quantum yield data and acid–base behavior suggest that the non-coordinated imidazole nitrogen tunes deactivation pathways.

© 2010 Published by Elsevier B.V.

1. Introduction

The complexes of ruthenium with bidentate, L₂-type heteroaromatic ligands exhibit rich photochemistry arising mainly from excited state electron-transfer reactions [1–5]. Among the panoply of such ligands, pyridylimidazoles are of interest because complexes of the two isomers, 4-(2'-pyridyl)-imidazole (4-pimH) and 2-(2'-pyridyl)-imidazole (2-pimH) (Fig. 1) should allow further investigation and discussion of the effects of subtle differences in

structure on the chemical properties of this molecular family. Moreover, the presence of non-coordinated, ionizable amines opens avenues of investigation into excited state acid–base behavior and proton-coupled electron transfer (PCET).

PimH isomeric differences were first described by Holmes et al. in a series of papers on association constant measurements and calorimetry of the reactions of 2-pimH and 4-pimH with various first-row transition elements [6–8]. These observations showed a general trend of weaker binding by 2-pimH than 4-pimH, with both being less strongly binding than bpy, a trend attributed to decreasing π-acceptor strength [7]. Holmes et al. [9] and Lions et al. [10] also noted an increase in the acidity of the pimH amine proton on complexation to metals, but did not quantify the change in pK_a.

* Corresponding author.

E-mail address: hgray@caltech.edu (H.B. Gray).

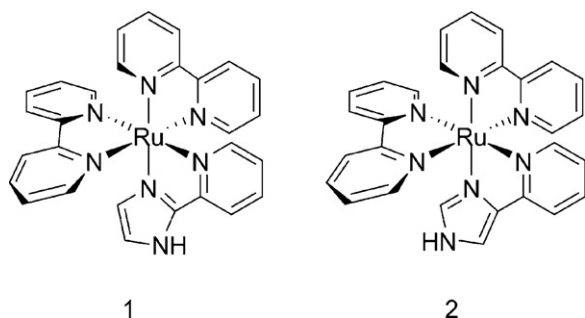


Fig. 1. Structures of Ru(bpy)₂(2-pimH) (1) and 4-pimH (2) complexes.

Later, Boggess and Martin reported a pK_a range of 8–10 for various [M(2-pimH)₃]²⁺ complexes and 13.4 for the free ligand [11]. Herein, we review the literature on Ru-pimH complexes with an emphasis on their photophysics and electrochemistry, and report an extension of Haga's work [12,13] on [Ru(bpy)₂(2-pimH)]²⁺ (1) including comparison to the heretofore unreported [Ru(bpy)₂(4-pimH)]²⁺ (2).

2. Properties of Ru^{II} complexes with pyridylimidazole and related ligands

Ru(II) complexes of 2-pimH, for which facile ligand syntheses exist, have been more extensively studied than those of 4-pimH. An enantiomerically enriched material was produced by synthesizing the homoleptic complex [Ru(2-pimH)₃]²⁺ [14–17] in the presence of (+)tartrate; its circular dichroism spectrum is similar to that of resolved [Ru(bpy)₃]²⁺ aside from a change in sign indicative of either a reversed Cotton effect or a shift from Δ to Λ as the favored enantiomer [14]. Cooling [Ru(2-pimH)₃]²⁺ to 77 K revealed photoluminescence; Braun et al. attributed its absence at room temperature to rapid ³MLCT (metal to ligand charge transfer) to ³MC (metal-centered) relaxation [15]. Braun observed the Ru^{III/II} couple, however, no electrochemical reduction of [Ru(2-pimH)₃]²⁺ is observable in acetonitrile, which speaks to the high-lying LUMO of the complex [15]. A cathodic shift of the Ru^{III/II} couple by 0.92 V was observed on full deprotonation of this complex [17]. Comparison of this shift with the 0.38 V cathodic shift observed by Haga on deprotonation of [Ru(bpy)₂(2-pimH)]²⁺ led the investigators to conclude that the stabilization of the higher oxidation state in the deprotonated homoleptic complex is mostly of electrostatic origin.

A detailed experimental and theoretical investigation has been reported on the effects of protonation states of a distal, non-coordinated imidazole motif on the electrochemistry and photophysics of Ru(bpy)₂(PhenImHPh) [PhenImHPh = 2-(3,5-di-*tert*-butylphenyl)imidazo[4,5-*f*]-[1,10]phenanthroline (3), Fig. 2] [18]. The investigators indicate that though the imidazole nitrogen atoms are not directly coordinated to the ruthenium, their protonation states dramatically perturb the excited state lifetimes of the molecule. Moreover, acid–base behavior allowed assignment of excited state localization to either the bpy or PhenImHPh ligands that was supported by theoretical results.

The isomeric complex [Ru(tpy)(bpy)imidazole]²⁺ and some derivatives have been prepared [19]; their reported photophysical properties have not been extensively interpreted but are broadly similar to 1 and 2 (*vide infra*) with differences due to the more extensively conjugated terpyridine ligand. Other monopyridylimidazole Ru complexes have been prepared with η^5 -cyclopentadienyl and phosphine [20], η^6 -benzene and chloride [21], and bis(β -diketonato) [22] ligands. The [Ru(2-pimH)(β -diketonato)₂] complexes display rich hydrogen atom transfer (HAT) chemistry at the free imidazole nitrogen that depends on the elec-

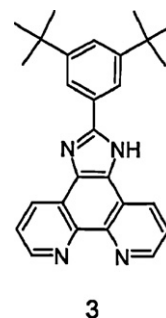


Fig. 2. Structure of 2-(3,5-di-*tert*-butylphenyl)imidazo[4,5-*f*]-[1,10]phenanthroline.

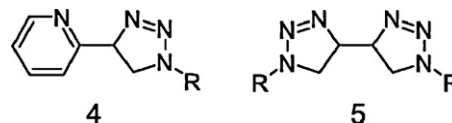


Fig. 3. Structures of 2'-(1,2,3-triazol-4-yl)pyridine (3) and 4,4'-bis(triazole) (4).

tronic nature of the ancillary ligands [22]. The general trends are as expected, with the more electron-withdrawing β -diketonate raising the MLCT energy, oxidation potential, and N–H bond dissociation energy (BDE) of the complex while lowering its pK_a .

The absorption spectra and reduction potentials of [RuL₃]²⁺ complexes featuring 2'-(1,2,3-triazol-4-yl)pyridine (4) and 4,4'-bis(triazole) (5) ligands (Fig. 3) have recently been reported [23]. The MLCT absorption energies of each complex correlate well with the separation of their first anodic and cathodic reduction potentials; this provides experimental corroboration of the electronic structural picture adopted for Ru polypyridine complexes possessing a largely metal-based HOMO beneath low-lying unoccupied ligand orbitals. Similarly, the properties of Ru(bpy)_{3-x}L_x²⁺ (*vide supra*) ($x=0-3$) complexes show systematic shifts as the bpy ligands are replaced with less donating 2,2'-bipyrazine and 2,2'-bipyrimidine ligands [24]. The $d\pi \rightarrow \pi^*$ absorptions undergo bathochromic shifting with increasing number of bpy ligands, behavior that is correlated with a decrease in Ru^{III/II} potentials. The optimization of a ruthenium bis-(methylbenzimidazole)pyridine complex for surface-tethered electrocatalytic water oxidation is an elegant demonstration of the application of redox tuning via ligand selection [25].

Despite the electronic tunability afforded by triazole, bipyrimidine, and bipyrazine, this set of ligands has the deficiency of being very weak bases at the distal nitrogen, as is exemplified by the pK_a values of 0.0 and 2.5 for the corresponding [Ru(NH₃)₅(C₄H₄N₂)]³⁺ complexes [26,27]. [Ru(bpy)₂(bpm)]²⁺ and [Ru(bpy)₂(bpz)]²⁺ show excited state pK_a shifts indicative of MLCT states involving the bipyrimidine or bipyrazine [24]; however, sequential protonation of ruthenium bipyrazine complexes requires strongly acidic conditions (>50% H₂SO₄) and leads to quenching of the luminescence [28]. In contrast, free imidazole has a pK_a of 14.2 [29] and its metal complexes are more acidic [30], leading to proton transfers under mild conditions. A similar shift has been observed in 2-pimH complexes [9–11].

Consequently, ruthenium complexes of pimH are of interest as they can undergo both acid–base and redox chemistry, (PCET) [31–33] and other hydrogen-bonding mediated interactions *via* the distal imidazole nitrogen. For example, the HAT kinetics of Ru^{II}(acac)₂(2-pimH) have recently been reported [34]. Intriguingly, the self-exchange reaction shows a k_H/k_D of only 1.5 despite a much higher kinetic isotope effect (KIE) of 23 in the reaction with 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO). If the proton source is a hydroxyl rather than an imidazole ligand, as is the case

Download English Version:

<https://daneshyari.com/en/article/1300248>

Download Persian Version:

<https://daneshyari.com/article/1300248>

[Daneshyari.com](https://daneshyari.com)