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Preparation and Electrochemistry of Biimidazolate Complexes of Ruthenium(II)

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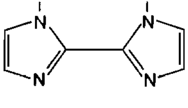
Abstract

The ruthenium(III) complex, $Ru(NH_3)_4(bimH_2)^{3+}$ ($bimH_2$ = 2,2′-biimidazole) has been prepared and characterized. The complex displays a ligand-to-metal charge-transfer (LMCT) transition at 640 nm. Reduction of the complex at a $pH < 6$, results in the formation of $Ru(NH_3)_4(bimH_2)^{2+}$. This Ru(II) complex has a metal-to-ligand charge-transfer (MLCT) transition at 407 nm. At $pH = 6$, the Ru(III) to Ru(II) reduction is accompanied by loss of a proton from the coordinated $bimH_2$ ligand.

Introduction

Recent work in our laboratory has focused on the development of bimetallic complexes consisting of a highly-absorbing photochemically inert antenna fragment, a reactive fragment which undergoes a useful photoreaction via an excited state that is inaccessible by visible light, and a communicative bridging ligand coupling the two centers [1]. Previous studies [1–3] have shown that the stability of the bimetallic complex is controlled as much by the overall charge on the complex as it is by the π-backbonding ability of the bridging ligand. Thus, in our design of bimetallic complexes for use in solar energy utilization studies, we have built in thermal stability by using bridging ligands capable of chelating both metal centers [2] and by reducing the overall charge of the complex by using anionic terminal ligands [3]. In this work we will modify our approach to charge reduction by using anionic bridging ligands derived from 2,2′-biimidazole($bimH_2$).

$bimH_2$ =



The mono deprotonated form, $bimH^-$, can be formed by removing one proton while bim^{2-}, formed by loss of two protons, is capable of binding two metal sites simultaneously in a bidentate fashion. The $Ru(NH_3)_4$ moiety was chosen as the metal center in these studies to understand the properties of $bimH_2$, $bimH^-$, and bim^{2-} by comparison to the well characterized $[Ru(NH_3)_4(bpy)]^{2+}$ [4], $[Ru(NH_3)_4(bpm)]^{2+}$ [3] and related ammineruthenium complexes of imidazole (imH) [5]. The pH dependent electrochemistry, electronic spectroscopy and synthetic studies will be used to study the stability of the various forms of $bimH_2$ when bound to the tetraammineruthenium center. These studies are described in this report.

Experimental

Materials

The ligand 2,2′-biimidazole was prepared by a previously reported procedure [6], and the identity and purity of the product was verified by mass spectrometry (Hewlett-Packard Model 5985). The starting complex, $[Ru(NH_3)_5(OH_2)](TFMS)_3$ ($TFMS^-$ = trifluoromethanesulfonate), was prepared in a stepwise fashion from $RuCl_3 \cdot 3H_2O$ (Johnson-Matthey) as described in refs. 7–9. All intermediate complexes had spectral properties that agreed with previous reports in the literature [10, 11].

The buffers used in the acid dependent measurements were prepared by mixing 0.1 M solutions of H_3PO_4 (Mallinkrodt), NaH_2PO_4 (Fisher), Na_2HPO_4 (Fisher) and Na_3PO_4 (Fisher). Water used in spectroscopic and electrochemical studies was deionized and distilled prior to use. All other materials were of reagent or analytical grade (where appropriate) and used as supplied.

Synthesis of $[Ru(NH_3)_4(bimH_2)](ClO_4)_3$

A 130 mg sample of $[Ru(NH_3)_4(OH_2)](TFMS)_3$ was dissolved in 25 ml of 100% ethanol, deoxygenated with argon and reduced with Zn/Hg amalgam in a pressure equalizing dropping funnel. A 4-fold excess of $bimH_2$ in 25 ml of 100% ethanol was stirred, heated, and deoxygenated with argon. The two reactants were mixed and stirred for four hours under argon. Within 30 min, the solution turned red, and

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after one hour became bluish-green. The solution was concentrated to ~5 ml on a rotary evaporator. The excess free ligand precipitated and was filtered off. Ether was added to precipitate a crude bluish-green material. The material was collected by filtration, dissolved in a minimum volume of ethanol, and precipitated by the addition of a saturated aqueous solution of $NaClO_4$. The precipitate was collected by filtration, washed with ethanol and ether, then dried under vacuum. The yield was 64 mg (53%). *Anal.* Calc. for $C_6H_{18}N_8Cl_3O_{12}Ru$: C, 11.97; H, 2.99; N, 18.62. Found: C, 12.08; H, 3.04; N, 18.60%.

Instrumentation

All electronic spectra were recorded on a Bausch and Lomb Spectronic 2000 using 1 cm matched quartz cells.

Cyclic and differential pulse voltammetries were carried out using an IBM Model EC 225/3A Voltammetric Analyzer. The glassy carbon working electrode was polished with alumina/water slurry prior to each series of scans. A platinum wire was used as the auxiliary electrode and a saturated potassium chloride calomel electrode was used as the reference electrode. The differential pulse measurements were carried out with a 10 mV/s scan rate and a 10 mV modulation amplitude. All voltammetry experiments were carried out on deoxygenated aqueous solutions which were 0.1 M in PO_4^{3-} and varied in pH. The pH values of the solution used were determined with an Orion Research Model 701A pH meter equipped with a combination glass/reference electrode. The response of the electrode was calibrated with two standard buffer solutions (Fisher) spanning the expected pH value of the solution.

Results and Discussion

Electrochemistry

The reduction of $[Ru(NH_3)_4(bimH_2)]^{3+}$, **I**, is chemically reversible on the cyclic voltammetry timescale, as shown by the symmetric anodic and cathodic traces of a typical voltammogram in Fig. 1. The pH dependence of the reduction potential is plotted in Fig. 2. In solutions more acidic than pH 6, the reduction potential is pH independent, indicating that the oxidized and reduced forms of **I** have the same proton content. Above pH 6, the reduction potential decreases by 59 mV/pH unit, which indicates the loss of a proton from one of the pyrrole nitrogens upon oxidation [5]. The −59 mV/pH unit slope and linearity (correlation coefficient = 0.993) of the $E_{1/2}$ *vs.* pH unit plot above pH 6 shows that the redox reaction is Nernstian in character [12].

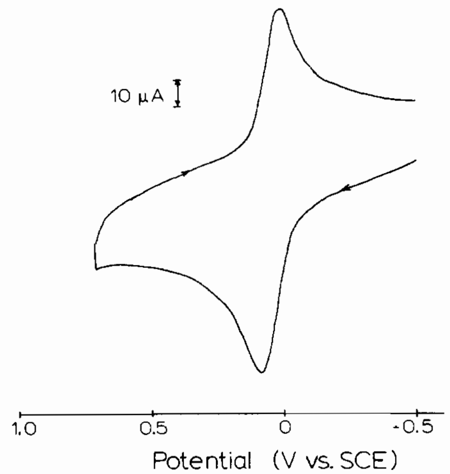

Fig. 1. Cyclic voltammogram of $Ru(NH_3)_4(bimH_2)^{3+}$ at room temperature in pH 2.2 phosphate buffered (0.1 M) solution *vs.* SCE. Scan rate = 100 mV/S.

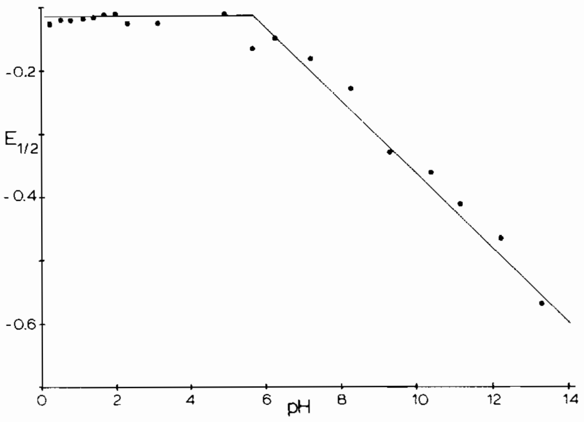

Fig. 2. $E_{1/2}$ *vs.* pH plot for the Ru(III)/Ru(II) couple for $Ru(NH_3)_4(bimH_2)^{3+}$, measured *vs.* SCE (see text). Filled circles correspond to experimental points and the line corresponds to the best fit. For pH > 5.8 slope = −0.059 V/pH unit with a correlation coefficient of 0.993.

In order to probe the absolute proton content of the species in solution, the proton acid nature of **I** was investigated. A small quantity (3–5 mg) of **I** was dissolved in several sets of deoxygenated aqueous solutions whose pH had been adjusted to values above (7.11 > pH > 5.80) or below (5.00 > pH > 4.23) the break point in the $E_{1/2}$ *vs.* pH unit plot with dilute NaOH or H_2SO_4, respectively. The pH change induced by adding **I** to these 10 ml solutions was measured and found to range from 2.79 > ΔpH > 1.62 for the solutions whose initial pH was above 6, and ΔpH < 0.30 for the solutions whose initial pH was below 6. The ΔpH values of 2.79 to 1.62 for the solutions of pH > 6 are consistent with the loss of a single proton from $[Ru(NH_3)_4(bimH_2)]^{3+}$, since the maximum ΔpH value expected for an equimolar amount of a strong monoprotic acid would be *ca.* 4 units. The relatively small ΔpH values observed for the solutions of pH 6 are consistent with no proton loss from **I**. Combining these observations with the $E_{1/2}$ *vs.* pH unit data leads to the assignment of the redox reaction occurring in solutions as,

$$\text{pH} < 6\ [\text{Ru(NH}_3)_4(\text{bimH}_2)]^{3+} + e^- \rightleftharpoons [\text{Ru(NH}_3)_4(\text{bimH}_2)]^{2+} \quad (1)$$

$$\text{pH} > 6\ [\text{Ru(NH}_3)_4(\text{bimH})]^{2+} + \text{H}^+ + e^- \rightleftharpoons [\text{Ru(NH}_3)_4(\text{bimH}_2)]^{2+} \quad (2)$$

Extrapolation of the lines obtained by least-squares analysis of the data shown in Fig. 2 yields a pK_a value for the equilibrium in eqn. 3 of 5.80.

$$[\text{Ru(NH}_3)_4(\text{bimH}_2)]^{3+} \rightleftharpoons [\text{Ru(NH}_3)_4(\text{bimH})]^{2+} + \text{H}^+ \quad (3)$$

Spectroscopy

The band maximum for the tetraammineruthenium biimidazole system and related imidazole, 2,2′-bipyridine (bpy) and bipyrimidine (bpm) complexes are summarized in Table I. The visible absorption spectrum of **I** is characterized by a band of 640 nm, which shifts to 660 nm in ethanol. In solutions more basic than pH:6, the band maximum shifts to 764 nm. A similar effect is observed for $[\text{Ru(NH}_3)_5(\text{imH})]^{3+}$, and was used to assign the electronic transition as a ligand-to-metal charge-transfer (LMCT) transition (imH → Ru(III)) [5], since deprotonation of imidazole or biimidazole ligand is expected for coulombic reasons to destabilize the highest occupied molecular orbital.

TABLE I. Electronic Spectral Data for Ammineruthenium Complexes of 2,2′-Biimidazole, Imidazole, 2,2′-Bipyridine, and 2,2′-Bipyrimidine[a]

Complex	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	Reference
$[\text{Ru(NH}_3)_5(\text{imH})]^{3+}$	430	250	5
$[\text{Ru(NH}_3)_4(\text{imH})_2]^{3+}$	435	347	5
$[\text{Ru(NH}_3)_5(\text{im})]^{2+}$	555	350	5
$[\text{Ru(NH}_3)_4(\text{bimH}_2)]^{3+}$	640	455	b
$[\text{Ru(NH}_3)_4(\text{bimH})]^{2+}$	764	462	b
$[\text{Ru(NH}_3)_5(\text{imH})]^{2+}$	280	2700	5
$[\text{Ru(NH}_3)_4(\text{bpy})]^{2+}$	366	5500	5
$[\text{Ru(NH}_3)_4(\text{bpm})]^{2+}$	402	8400	2
$[\text{Ru(NH}_3)_4(\text{bimH}_2)]^{2+}$	407	2700	b

[a]Aqueous solution, room temperature. [b]This work.

Spectrophotometric titration of **I** yields a pK_a value for the equilibrium in eqn. 3 of 5.65, which is consistent with the value obtained from voltammetry. The free ligand has a pK_a of 11.5 [6], which indicates that complexation of bimH_2 to $[\text{Ru}^{\text{III}}(\text{NH}_3)_4]$ increases the acidity of this ligand by more than six orders of magnitude. This change in acidity is considerably more pronounced than that observed for imidazole bound to either $\text{Ru}^{\text{III}}(\text{NH}_3)_5$ or iron porphyrins. In porphyrin complexes, pK_a values of 10.31 [6] and 10.45 [13] have been reported, as compared to the imidazole free ligand value of 14.2. A similar effect is observed for pyrazine [14], which is *ca.* 1.5 orders of magnitude more acidic bound as $[\text{Ru(NH}_3)_5(\text{pyrazine})]^{3+}$ [15] than free. These data are summarized in Table II.

TABLE II. pK_a Values for Ammineruthenium Complexes of 2,2′-Biimidazole, Imidazole, Pyrazine, and the Free Ligands[a]

Molecule	pK_a	Reference
Imidazole	14.2	13
2,2′-Biimidazole	11.5	6
$[\text{Ru(NH}_5)_5(\text{imH})]^{3+}$	8.9	5
$[\text{Ru(NH}_3)_4(\text{bimH}_2)]^{3+}$	5.65[b] 5.80[c]	d
Pyrazine	0.6	15
$[\text{Ru(NH}_3)_5(\text{pyrazine})]^{3+}$	−0.8	14

[a]Aqueous solution, room temperature. [b]Determined spectrophotometrically. [c]Determined electrochemically. [d]This work.

The larger increase in ligand acidity and lower energy for the LMCT band in **I**, compared to imH derivatives, is probably due to a better energy match between the metal orbitals of the $\text{Ru}^{\text{III}}(\text{NH}_3)_4$ fragment and the p_π orbitals of the bimH_2 ligand. This is particularly evident when the wavelength maximum of **I** is compared to that of its close analog, $[\text{Ru(NH}_3)_4(\text{imH})_2]^{3+}$. Substitution of imH for NH_3 has little effect on the wavelength maximum or extinction coefficient. Coupling the two imH ligands at the 2 position to give bimH_2 has a profound effect on the wavelength maximum, consistent with a decreased energy gap between the p_π levels on bimH_2 and the partially filled d_π orbitals on $\text{Ru}^{\text{III}}(\text{NH}_3)_4$. This would result in increased electron delocalization of the p_π electrons onto the metal, which would stabilize the deprotonated form of bimH_2.

The Ru(II) species, $[\text{Ru(NH}_3)_4(\text{bimH}_2)]^{2+}$, was generated *in situ* [5] with Zn/Hg amalgam. The absorption maximum shifts to higher energy (407 nm) than the Ru(III) analog. The reduction to Ru(II) fills the d_π orbitals and raises the energy of the ruthenium atomic orbitals due to a reduction in positive charge. This results in a shift of the d_π orbital energy away from the p_π orbitals of $bimH_2$ and toward the $p_{\pi*}$ orbitals of this ligand. Thus electronic transition at 407 nm for the Ru(II) complex is assigned as a metal-to-ligand, charge-transfer (MLCT) transition from the filled d_π orbitals on Ru(II) to the $p_{\pi*}$ orbitals on $bimH_2$. Analogous MLCT transitions have been observed and assigned for $Ru(NH_3)_4(bpy)^{2+}$ [16, 17] (bpy = 2,2′-bipyridine) and $Ru(NH_3)_4(bpm)^{2+}$ [2] absorption bands. Also, an increase in electron density in the donor orbital should yield a red shift in the absorption maximum if the nature of the transition was the same for Ru(II) and Ru(III) species.

The MLCT and LMCT transitions for $Ru(NH_3)_4L^{2+}$ and $Ru(NH_3)_4L^{3+}$ complexes (L = $bimH_2$, bpy, bpm) show a similarity in the Ru(II) complex with all the MLCT transitions occurring between 366 and 407 nm. However, only the $bimH_2$ also has a low energy LMCT (640 nm) in the Ru(III) form. The relatively low energies for both $bimH_2$ systems suggests that the complex may be useful in a catalytic cycle such as the following:

$$\begin{array}{c} X^{n} \longrightarrow X^{n+1} \\ \mathrm{Ru(NH_3)_4(bimH_2)^{3+}} \underset{h\nu',\mathrm{MLCT}}{\overset{h\nu,\mathrm{LMCT}}{\rightleftarrows}} \mathrm{Ru(NH_3)_4(bimH_2)^{2+}} \\ Y^{n-1} \longleftarrow Y^{n} \end{array}$$

Finally, the $Ru(NH_3)_4(bimH_2)^{3+}$ LMCT (640 nm) to $Ru(NH_3)_4(bimH_2)^{2+}$ MLCT (407 nm) shift parallels the shift from 430 to 280 nm for $Ru(NH_3)_5(imH)^{3+/2+}$, respectively. Presumably, the same assignments can be made for the nature of the transitions in the imH system. The higher energy transitions in the imH system *vs.* the $bimH_2$ system is due to increased number of coordination sites occupied by the heterocycle and increased π stability of the heterocycle (due to larger delocalization) in the latter complex.

Conclusion

The nature of the '$Ru(NH_3)_4$' metal center prevents the solution from becoming basic enough to deprotonate bound $bimH_2$. This eliminates the possibility of forming bimetallic complexes between ruthenium ammines and other metal centers with bim^{2-} as the bridging ligand. Bridging two metal sites using bim^{2-} can be accomplished using '$Ru(bpy)_2$' as the metal center [18] but only under extremely basic (pH 12) conditions. However, the nature of Ru(III) LMCT and Ru(II) MLCT transitions does make the $bimH_2$ complexes outstanding prospects for catalytic systems. The proton coupled electron transfer for $Ru(NH_3)_4(bimH_2)^{2+}$ shown in eqn. 2 for solutions above pH 5.6 makes this species potentially a very rapid pH gradient electrical switch.

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