

An Electrochemical, Spectroscopic, and Potentiometric Study of the Reactions of the Complex $[\text{Ru}^{(\text{III}/\text{II})}(\text{HEDTA})(\text{H}_2\text{O})]^{0/-}$ with the Ligand Diacetyl β -Piridyl(2) Methylimin (DPMH)

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Received: April 30, 1994; August 16, 1994

O complexo $[\text{Ru}^{(\text{II})}(\text{HEDTA})(\text{H}_2\text{O})]^-$ foi obtido *in situ* por redução do complexo $[\text{Ru}^{(\text{III})}(\text{HEDTA})(\text{H}_2\text{O})]$ com amálgama de zinco e titulado com o ligante tridentado diacetil-monooxima- β -piridil(2)-metilimina (DPMH), formando as espécies $[\text{Ru}^{(\text{II})}(\text{HEDTA})(\text{DPMH})]^-$ e $[\text{Ru}^{(\text{II})}(\text{DPMH})_2]^{2+}$. Os complexos mostraram bandas de transferência de carga metal ligante em 516 nm e 367 nm. As constantes totais de formação para os complexos de $\text{Ru}^{(\text{II})}$ foram determinadas pelos métodos espectrofotométrico e voltamétrico e para o complexo $\text{Ru}^{(\text{III})}$, pelo método potenciométrico. As interações dos complexos de rutênio com o ligante DPMH foram analisados.

The $[\text{Ru}^{(\text{II})}(\text{HEDTA})(\text{H}_2\text{O})]^-$ complex was obtained *in situ* by the zinc amalgam reduction of $[\text{Ru}^{(\text{III})}(\text{HEDTA})(\text{H}_2\text{O})]$. Under these reduction reaction conditions the product $[\text{Ru}^{(\text{II})}(\text{HEDTA})(\text{H}_2\text{O})]^-$ reacts with the tridentated ligand DPMH (diacetyl-monooxim- β -pyridyl-ethylimin) to form the $[\text{Ru}^{(\text{II})}(\text{HEDTA})(\text{DPMH})]^-$ and $[\text{Ru}^{(\text{II})}(\text{DPMH})_2]^{2+}$ complexes. These complexes show metal to ligand charge transfer bands in 516 nm and 367 nm. The total formation constants were determined by spectrophotometric and voltammetric methods for the $\text{Ru}^{(\text{II})}$ complex and the potentiometric method for the $\text{Ru}^{(\text{III})}$ complex. The results can be rationalized on the basis of the interaction between the ruthenium complex and the DPMH ligand.

Keywords: equilibrium constants, diacetyl-monooxim- β -pyridyl-ethylimin, $[\text{Ru}^{(\text{II})}(\text{HEDTA})(\text{H}_2\text{O})]^-$

Introduction

Systematic studies of the reactions of the complex $\text{Ru}^{(\text{III}/\text{II})}\text{EDTA}$ with sulfur or nitrogen ligands of biologic or catalytic interest have been carried out by many authors¹⁻⁵. These studies have contributed to a better understanding of the reactions of these complexes in the presence of ligands, such as aminoacids. Potentiometric titrations have indicated that the $\text{Ru}^{(\text{III})}$ complex with EDTA are pentacoordinated in an aqueous solution, pH 3-6, and the sixth coordination site is occupied by a water molecule that can be easily substituted by nitrogenated ligands⁶. The aim of this work is to study the reaction patterns of the complex

$[\text{Ru}^{(\text{III}/\text{II})}(\text{HEDTA})(\text{H}_2\text{O})]^{n-}$ with a diacetyl-monooxim- β -pyridyl-methylimin (DPMH) ligand by spectrophotometric, electrochemical and potentiometric methods.

Experimental

The complex $[\text{Ru}^{(\text{III})}(\text{HEDTA})(\text{H}_2\text{O})]$ was synthesized according to the procedure previously described in the literature⁷. The ligand diacetyl-monooxim- β -pyridyl-methylimin was prepared by the method described by Levy⁸. An elemental analysis showed a good agreement between the experimental and calculated results, as shown in Table 1.

Spectrophotometric titration was carried out in an HP 8450A Diode-Array spectrophotometer, in an aqueous so-

Table 1. Elemental analysis.

	% C		% H		% N	
	calcd.	found	calcd.	found	calcd.	found
RuC ₁₀ H ₂₆ N ₂ O ₁₃ Cl ₂	21.71	21.74	4.55	4.37	5.06	4.76
C ₁₀ H ₁₃ N ₃ O	62.83	62.41	6.80	6.24	21.98	21.40

lution, with a hydrogen phthalate buffer and ionic strength 0.1 M, in a quartz cell with an optical path of 1.0 cm.

The potentiometric data were obtained in a Micronal pH meter, model 375, with a glass electrode and calomel as a reference electrode. The pH values were obtained at 25.00 ± 0.05 °C in a glass cell under an argon atmosphere. The pH meter was standardized with HCl standard solution, and the 0.1 M ionic strength was adjusted with KCl. To determine the stability constants, a solution was prepared containing 0.1022 mmol of the complex $H_2[Ru^{(III)}(HEDTA)Cl_2] \cdot 3H_2O$, 0.19565 mmol of DPMH and 0.8932 mmol of HCl. The titrant solution (CO₂ free) of KOH 0.0988 M was added in increments of 0.100 mL to obtain over 86 equilibrium points. Ligand protonation, metal chelate protonation and stability constants were calculated using the program Best⁹. The cyclic voltammetric measurements were obtained on a cyclic voltammeter from Bioanalytical System Inc., mod. CV-27, coupled with an X-Y plotter from Houston Instruments, mod. Omnigrafic 100. A three-electrode system was utilized, with vitreous carbon as the working electrode, KCl saturated Ag/AgCl as the reference electrode, and an auxiliary electrode of platinum. The potentials were referenced to SHE, adding 0.204 V to the potentials obtained against Ag/AgCl in a saturated solution of KCl. The voltammetric titration of the complex of Ru^(III) (1×10^{-3} M) obtained by reduction of the complex $[Ru^{(III)}(HEDTA)(H_2O)]$ with an amalgam was carried out in an aqueous solution, deaired with argon in a biphthalate buffer pH 5.15 and ionic strength 0.1 M. A ligand solution DPMH (4×10^{-2} M) dissolved in ethanol was added in aliquots of 0.1 mL.

Results and Discussion

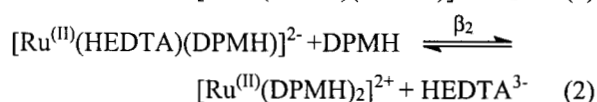
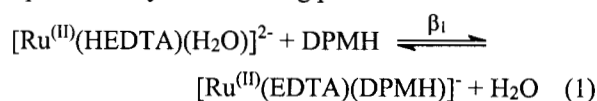
In this study we investigated the substitution of the ligand EDTA in the complex $[Ru^{(III/II)}(HEDTA)(H_2O)]^n$ by spectrophotometric, voltammetric and potentiometric titration with the α -diiminic ligand DPMH.

The stability constants for the formation of metallic complexes is utilized as an effective measurement of the affinity of a ligand for the metallic ion.

Spectrophotometric titration

The product $[Ru^{(II)}(DPMH)_2]^{2+}$, obtained by the reaction of the complex $[Ru^{(III)}(HEDTA)(H_2O)]^{2-}$ with the ligand DPMH, is stable and can easily be identified by the electronic spectrum, inasmuch as it shows metal-ligand charge

transfer bands $d_{\pi}-p_{\pi}^*$ (Ru \rightarrow pyridine) in 367 nm, $\epsilon = 4.8 \times 10^3$ M⁻¹ cm⁻¹. The charge transfer band observed in 516 nm $\epsilon = 9.5 \times 10^3$ M⁻¹ cm⁻¹ corresponds to the Ru \rightarrow α -diiminic charge transfer (Fig. 1). The transitions observed are in agreement with the values reported in the literature for complexes with α -diiminic ligands^{8,10} and can be represented by the following pattern of reactions:



The constants for complexation $\beta_1 = 6.5 \times 10^3$ and $\beta_2 = 2.41 \times 10^2$, were calculated by the McConnell method¹¹ (Eq. 3), and are compatible with those obtained for the reaction of the complex Fe(HEDTA) with the ligands DPMH and DPEH¹².

$$\frac{[M] \cdot [L]}{A_f - A_i} = \frac{[M] + [L]}{\epsilon_f - \epsilon_i} + \frac{1}{\beta(\epsilon_f - \epsilon_i)} \quad (3)$$

Cyclic voltammetry

In the cyclic voltammogram shown in Fig. 2, we observed the presence of three different species whose $E_{1/2}^0$ values are 0.05 V vs. SHE for the complex $[Ru^{(III/II)}$

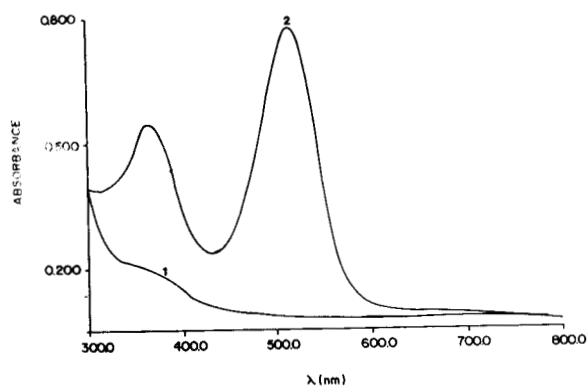


Figure 1. Spectrophotometric titration of $[Ru^{(III)}(HEDTA)(H_2O)]^-$ complex with DPMH ligand in aqueous solution. pH 5.15 biphthalate buffer I = 0.1 M. T = 25 °C.

1 - $[Ru^{(III)}(HEDTA)(H_2O)]^-$ complex.

2 - $[Ru^{(II)}(DPMH)_2]^{2+}$ complex.

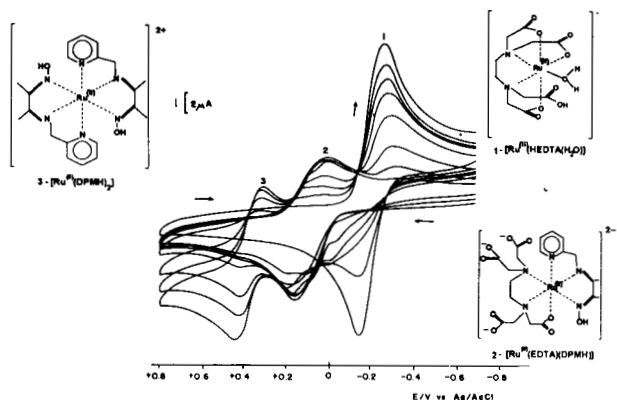


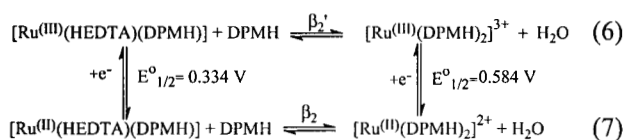
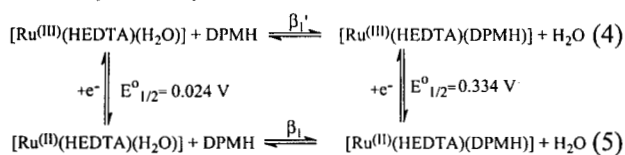
Figure 2. Voltammetric titration of $[\text{Ru}^{\text{III}}(\text{HEDTA})(\text{H}_2\text{O})]^-$ complex with DPMH ligand in aqueous solution. pH 5.15 biphthalate buffer $I = 0.1 \text{ M}$. $V = 40 \text{ mV/s}$, $T = 25 \text{ }^\circ\text{C}$.

- 1 - $[\text{Ru}^{\text{III/II}}(\text{HEDTA})(\text{H}_2\text{O})]^-$
 2 - $[\text{Ru}^{\text{III/II}}(\text{EDTA})(\text{DPMH})]^-$
 3 - $[\text{Ru}^{\text{III/II}}(\text{DPMH})_2]^{2+}$ complex.

$(\text{HEDTA})(\text{H}_2\text{O})]^{2-}$, 0.334 V vs. SHE for the species $[\text{Ru}^{\text{III/II}}(\text{HEDTA})(\text{DPMH})]^-$, and 0.584 V vs. SHE for the complex $[\text{Ru}^{\text{III/II}}(\text{DPMH})_2]^{2+}$.

After several of hours in the presence of a great excess of ligand DPMH, the cyclic voltammogram showed only the cathodic and anodic peaks, corresponding to the species $[\text{Ru}^{\text{III}}(\text{DPMH})_2]^{2+}$, as shown in (Fig. 3).

Thermodynamic cycle



The log of $\beta_1' = 9.07$ and the log of $\beta_2' = 13.22$ for the Ru^{III} complex were calculated, based on $E^{\circ}_{1/2}$ data, with the aid of a thermodynamic cycle, (Reactions 4-7) and Eqs. 8 and 9.

$$E_{[\text{Ru}^{\text{III/II}}(\text{EDTA})]} = E_{[\text{Ru}^{\text{III/II}}(\text{EDTA})(\text{DPMH})]} + RT/F \ln \beta_1 / \beta_1' \quad (8)$$

$$E_{[\text{Ru}^{\text{III/II}}(\text{EDTA})]} = E_{[\text{Ru}^{\text{III/II}}(\text{EDTA})(\text{DPMH})_2]} + RT/F \ln \beta_2 / \beta_2' \quad (9)$$

Potentiometric titration

The stability constants β_1' and β_2' for the reactions of the complex $[\text{Ru}^{\text{III}}(\text{HEDTA})(\text{H}_2\text{O})]^{2-}$ with the ligand DPMH were determined by the potentiometric method, with the aim of making a comparison between the electrochemical and spectrophotometric data. The species distri-

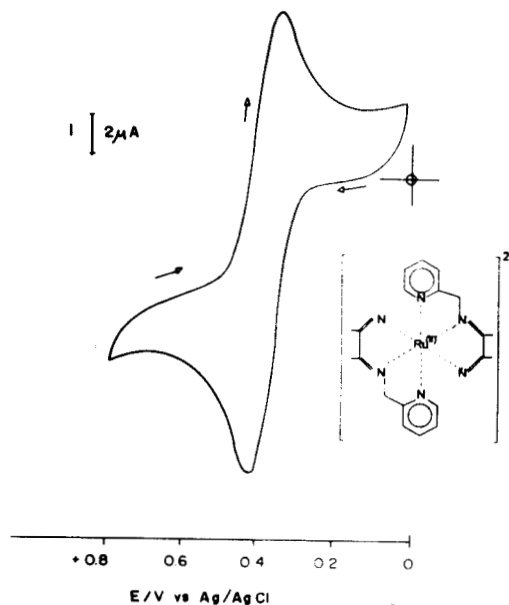
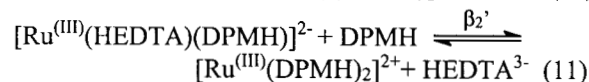
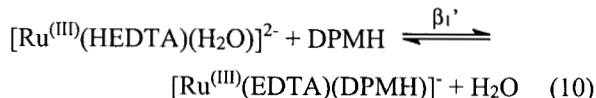


Figure 3. Cyclic Voltammogram of $[\text{Ru}^{\text{III}}(\text{DPMH})_2]^{2+}$ complex in aqueous solution. pH 5.15 biphthalate buffer $I = 0.1 \text{ M}$. Obtained in the presence of an excess of ligand DPMH and after a number of hours.

butions of the complexes formed are presented in Fig. 4. β_1' and β_2' are defined by reactions 10 and 11:



$$\beta_1' = \text{size}9.5 \left\{ \frac{[\text{Ru}^{\text{III}}(\text{EDTA})(\text{DPMH})]^-}{[\text{Ru}^{\text{III}}(\text{HEDTA})(\text{H}_2\text{O})]^{2-} [\text{DPMH}]} \right\} \quad (12)$$

$$\beta_2' = \text{size}9.5 \left\{ \frac{[\text{Ru}^{\text{III}}(\text{DPMH})_2]^{2+}}{[\text{Ru}^{\text{III}}(\text{HEDTA})(\text{H}_2\text{O})]^{2-} [\text{DPMH}]^2} \right\} \quad (13)$$

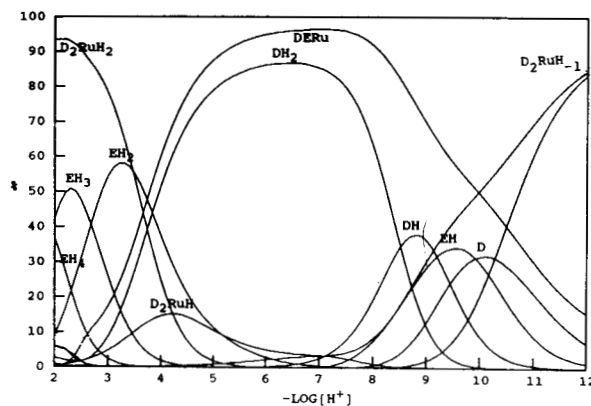


Figure 4. Metal ion, ligand and complex species distribution curves for the $[\text{Ru}^{\text{III}}(\text{HEDTA})(\text{H}_2\text{O})]^- / \text{DPMH}$ system as a function of $-\log [\text{H}^+]$. $I = 0.1 \text{ M}$; KCl , $T = 25 \text{ }^\circ\text{C}$. $\text{DH}_2 = [\text{DPMH}_2]^+$, $\text{DH} = [\text{DPMH}]$, $\text{D} = [\text{DPM}]$, $\text{EH}_2 = \text{H}_2\text{EDTA}^{2-}$, $\text{EH} = \text{HEDTA}^{3-}$, $\text{DERu} = [\text{Ru}^{\text{III}}(\text{EDTA})(\text{DPMH})]^-$, $\text{D}_2\text{RuH} = [\text{Ru}^{\text{III}}(\text{DPMH})(\text{DPM})]^+$ and $\text{D}_2\text{RuH}_2 = [\text{Ru}^{\text{III}}(\text{DPMH})_2]^{3+}$.

Table 2. Results of $\log \beta_1'$ and $\log \beta_2'$ for the titration of the complex $[\text{Ru}^{\text{III}}(\text{HEDTA})(\text{H}_2\text{O})]^{2-}$ with the ligand DPMH.

Method	Log β_1'	Log β_2'
Voltammetry /Spectroscopy	9.07	13.22
Potentiometry	8.43	13.81

$\log \beta_1' = 10.60$ and $\log \beta_2' = 13.58$ for the reactions to substituting ligand EDTA for ligand DPMH in the complex $[\text{Ru}^{\text{III}}(\text{HEDTA})(\text{H}_2\text{O})]^{2-}$, calculated with the aid of the program Best 7¹².

Conclusion

The stability constants β_1' and β_2' calculated by potentiometric and cyclic voltammetric/spectroscopic methods have shown good consistency, as can be seen in Table 2. The changes in the oxidation state of the metallic ion of the complex Ru^{III} EDTA, to Ru^{II} and Ru^{I} facilitates the substitution of the EDTA ligand with the ligand DPMH, which has double α -diiminic bonding which can couple to the pyridinic ring. This fact occurs in conjunction with the entropic effect of EDTA. Since Ru^{II} is a metallic ion with the characteristics of a moderate soft acid, it allows the substitution of the ligand EDTA (hard base) with the ligand DPMH (soft base), as foreseen in Pearson's theory¹³. The α -diiminic bonding of the ligand DPMH, due to its π -acceptor ability, displaces the oxidation reduction potential of the complex $[\text{Ru}^{\text{II}}(\text{DPMH})_2]^{2+}$ to a region of more positive values, stabilizing the lowest oxidation state.

Acknowledgments

We thank CNPq, Finep and CAPES for financial support.

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