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

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O complexo $[\text{Ru}^{(II)}(\text{HEDTA})(\text{H}_2\text{O})]^+$ foi obtido in situ por redução do complexo
$[\text{Ru}^{(II)}(\text{HEDTA})(\text{H}_2\text{O})]$ com amálgama de zinco e titulado com o ligante tridentado diacel-
monoxoxima-$\beta$-piridil(2)-metilimin (DPMH), formando as espécies $[\text{Ru}^{(II)}(\text{HEDTA})(\text{DPMH})]^+$ e
$[\text{Ru}^{(II)}(\text{DPMH})]^2+$. 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 $\text{Ru}^{(II)}$ foram determinadas pelos
métodos espectrofotométrico e voltamétrico e para o complexo $\text{Ru}^{(III)}$, pelo método potenciométrico.
As interações dos complexos de rutênio com o ligante DPMH foram analisados.

The $[\text{Ru}^{(II)}(\text{HEDTA})(\text{H}_2\text{O})]^+$ complex was obtained in situ by the zinc amalgam reduction of
$[\text{Ru}^{(II)}(\text{HEDTA})(\text{H}_2\text{O})]$. Under these reduction reaction conditions the product
$[\text{Ru}^{(III)}(\text{HEDTA})(\text{H}_2\text{O})]^+$ reacts with the tridentated ligand DPMH (diacetyl-monoxoxim-$\beta$-piridyl-
ethylimin) to form the $[\text{Ru}^{(III)}(\text{HEDTA})(\text{DPMH})]^+$ and $[\text{Ru}^{(II)}(\text{DPMH})]^2+$ complexes. These com-
plexes 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 $\text{Ru}^{(II)}$ complex
and the potentiometric method for the $\text{Ru}^{(III)}$ complex. The results can be rationalized on the basis
of the interaction between the ruthenium complex and the DPMH ligand.

Keywords: equilibrium constants, diacetyl-monoxoxim-$\beta$-piridyl-ethylimin, $[\text{Ru}^{(III)}$
$(\text{HEDTA})(\text{H}_2\text{O})]^+$. 

Introduction

Systematic studies of the reactions of the complex $\text{Ru}^{(III/II)}$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 $\text{Ru}^{(III)}$ 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 ligands5. The aim of
this work is to study the reaction patterns of the complex
$[\text{Ru}^{(III/II)}(\text{HEDTA})(\text{H}_2\text{O})]^n-$ with a diacetyl-monoxoxim-$\beta$-
piridil-methylimin (DPMH) ligand by spectrophotometric,
electrochemical and potentiometric methods.

Experimental

The complex $[\text{Ru}^{(III)}(\text{HEDTA})(\text{H}_2\text{O})]$ was synthesized
according to the procedure previously described in the litera-
ture7. The ligand diacetyl-monoxoxim-$\beta$-piridil-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-
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 H₂[Ru(HEDTA)Cl₂]·3H₂O, 0.19565 mmol of DPMH and 0.8932 mmol of HCl. The titration 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 voltameter from Bioanalytical System Inc., mod. CV-27, coupled with an X-Y plotter from Houston Instruments, mod. Omnicronic 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 Ru²⁺ (1 x 10⁻³ M) obtained by reduction of the complex [Ru²⁺(HEDTA)(H₂O)] with an amalgam was carried out in an aqueous solution, deaerated with argon in a biphthalate buffer pH 5.15 and ionic strength 0.1 M. A ligand solution DPMH (4 x 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 [Ru²⁺(HEDTA)(H₂O)]⁶⁻ 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 [Ru²⁺(DPMH)]¹²⁺, obtained by the reaction of the complex [Ru²⁺(HEDTA)(H₂O)]⁶⁻ with the ligand DPMH, is stable and can easily be identified by the electronic spectrum, inasmuch as it shows metal-ligand charge transfer bands δₓ-pₓ⁺ (Ru → pyridine) in 367 nm, ε = 4.8 x 10³ M⁻¹ cm⁻¹. The charge transfer band observed in 516 nm ε = 9.5 x 10³ M⁻¹ cm⁻¹ corresponds to the Ru → α-diiminic charge transfer (Fig. 1). The transitions observed are in agreement with the values reported in the literature for complexes with α-diiminic ligands⁸,¹⁰ and can be represented by the following pattern of reactions:

\[
[Ru²⁺(HEDTA)(H₂O)]²⁻ + DPMH \xrightarrow{\beta₁} [Ru²⁺(DPMH)]²⁻ + H₂O
\]

\[
[Ru²⁺(HEDTA)(DPMH)]²⁻ + DPMH \xrightarrow{\beta₂} [Ru²⁺(DPMH)₂]²⁻ + HEDTA³⁻ \tag{2}
\]

The constants for complexation \(\beta₁ = 6.5 x 10³\) and \(\beta₂ = 2.41 x 10²\), 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.

\[
\frac{[M][L]}{A_i - A_t} = \frac{[M] + [L]}{ε_f - ε_i} + \frac{1}{β(ε_f - ε_i)} \tag{3}
\]

Cyclic voltammetry

In the cyclic voltammogram shown in Fig. 2, we observed the presence of three different species whose E¹/₂ values are 0.05 V vs. SHE for the complex [Ru²⁺(HEDTA)]⁶⁻.
Figure 2. Voltammetric titration of [Ru\textsuperscript{II}(HEDTA)(H\textsubscript{2}O)]\textsuperscript{+} complex with DPMH ligand in aqueous solution, pH 5.15 biphasate buffer 1 = 0.1 M. V = 40 mV/s, T = 25 °C.

1. [Ru\textsuperscript{II}(HEDTA)(H\textsubscript{2}O)]\textsuperscript{+}
2. [Ru\textsuperscript{II}(EDTA)(DPMH)]\textsuperscript{+}
3. [Ru\textsuperscript{II}(DPMH)]\textsuperscript{2+}

(HEDTA)(H\textsubscript{2}O)]\textsuperscript{2+}, 0.334 V vs. SHE for the species [Ru\textsuperscript{II}(HEDTA)(DPMH)]\textsuperscript{+} and 0.584 V vs. SHE for the complex [Ru\textsuperscript{II}(DPMH)]\textsuperscript{2+}.

After several 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 [Ru\textsuperscript{II}(DPMH)]\textsuperscript{2+}, as shown in (Fig. 3).

**Thermodynamic cycle**

\[
\begin{align*}
[Ru^{III}(HEDTA)(H_2O)]^+ + DPMH \rightleftharpoons [Ru^{III}(HEDTA)(DPMH)]^+ + H_2O & (4) \\
E^{\prime}_{1/2} = 0.024 V & \\
[Ru^{II}(HEDTA)(H_2O)]^+ + DPMH \rightleftharpoons [Ru^{II}(HEDTA)(DPMH)]^+ + H_2O & (5) \\
E^{\prime}_{1/2} = 0.334 V & \\
[Ru^{II}(HEDTA)(DPMH)]^+ + DPMH \rightleftharpoons [Ru^{II}(DPMH)]^{2+} + H_2O & (6) \\
E^{\prime}_{1/2} = 0.334 V & \\
[Ru^{II}(DPMH)]^{2+} + DPMH \rightleftharpoons [Ru^{II}(DPMH)]^{2+} + H_2O & (7) \\
E^{\prime}_{1/2} = 0.584 V &
\end{align*}
\]

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

\[
E_{[Ru^{III}(EDTA)]} = E_{[Ru^{III}(EDTA(DPMH)]} + RT/F \ln \beta_1/\beta_1^\prime (8)
\]

\[
E_{[Ru^{III}(EDTA)]} = E_{[Ru^{III}(DPMH)]} + RT/F \ln \beta_2/\beta_2^\prime (9)
\]

**Potentiometric titration**

The stability constants \(\beta_1\) and \(\beta_2\) for the reactions of the complex [Ru\textsuperscript{II}(HEDTA)(H\textsubscript{2}O)]\textsuperscript{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 [Ru\textsuperscript{III}(DPMH)]\textsuperscript{2+} complex in aqueous solution, pH 5.15 biphasate buffer 1 = 0.1 M. Obtained in the presence of an excess of ligand DPMH and after a number of hours.

The results of the complexes formed are presented in Fig. 4. \(\beta_1\) and \(\beta_2\) are defined by reactions 10 and 11:

\[
[Ru^{III}(HEDTA)(H_2O)]^{2+} + DPMH \rightleftharpoons [Ru^{III}(HEDTA)(DPMH)]^+ + H_2O & (10) \\
[Ru^{III}(EDTA)(DPMH)]^+ + DPMH \rightleftharpoons [Ru^{III}(DPMH)]^{2+} + HEDTA & (11)
\]

\[\beta_1 = \text{size 9.5} \left[\frac{[Ru(HEDTA)(DPMH)]^+}{[Ru(HEDTA)(H_2O)][DPMH]}\right] (12)\]

\[\beta_2 = \text{size 9.5} \left[\frac{[Ru(DPMH)]^2^+}{[Ru(HEDTA)(H_2O)][DPMH]}\right] (13)\]

Figure 4. Metal ion, ligand and complex species distribution curves for the [Ru\textsuperscript{III}(HEDTA)(H\textsubscript{2}O)] / DPMH system as a function of -log [H\textsuperscript{+}]; 1 = 0.1 M; KCl, T = 25 °C. DH\textsuperscript{III} = [DPMH]\textsuperscript{2+}, DH\textsuperscript{II} = [DPMH], D\textsuperscript{+} = [DPMH], EH\textsuperscript{II} = [HEDTA]\textsuperscript{2+}, DE\textsuperscript{III} = [Ru\textsuperscript{III}(EDTA)(DPMH)], D\textsubscript{2}Ru\textsubscript{II} = [Ru\textsuperscript{II}(DPMH)]\textsuperscript{2+} and D\textsubscript{3}RuH\textsubscript{2} = [Ru\textsuperscript{II}(DPMH)]\textsuperscript{2+}. 

\[
\begin{align*}
\beta_1 = \text{size 9.5} & \left[\frac{[Ru(HEDTA)(DPMH)]^+}{[Ru(HEDTA)(H_2O)][DPMH]}\right] (12) \\
\beta_2 = \text{size 9.5} & \left[\frac{[Ru(DPMH)]^2^+}{[Ru(HEDTA)(H_2O)][DPMH]}\right] (13)
\end{align*}
\]
Table 2. Results of $\log \beta_1'$ and $\log \beta_2'$ for the titration of the complex [Ru(III)(HEDTA)(H₂O)]²⁺ with the ligand DPMH.

<table>
<thead>
<tr>
<th>Method</th>
<th>$\log \beta_1'$</th>
<th>$\log \beta_2'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltammetry /Spectroscopy</td>
<td>9.07</td>
<td>13.22</td>
</tr>
<tr>
<td>Potentiometry</td>
<td>8.43</td>
<td>13.81</td>
</tr>
</tbody>
</table>

Log $\beta_1' = 10.60$ and log $\beta_2' = 13.58$ for the reactions to substituting ligand EDTA for ligand DPMH in the complex [Ru(III)(HEDTA)(H₂O)]²⁺, calculated with the aid of the program Best 7¹².

Conclusion

The stability constants $\beta_1'$ and $\beta_2'$ 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(II) EDTA, to Ru(III) and Ru(IV) facilitates the substitution of the EDTA ligand with the ligand DPMH, which has double $\alpha$-diimine bonding which can couple to the pyridinic ring. This fact occurs in conjunction with the entropic effect of EDTA. Since Ru(III) 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 $\alpha$-diimine bonding of the ligand DPMH, due to its $\pi$-acceptor ability, displaces the oxidation reduction potential of the complex [Ru(III)(DPMH)]²⁺ to a region of more positive values, stabilizing the lowest oxidation state.

Acknowledgments

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References