

CITY UNIVERSITY OF HONG KONG

香港城市大學

Synthesis and Characterization of Ruthenium

Complexes as Redox Mediators of Biosensors

生物傳感器的鈦配合物氧化還原媒介的
合成及表徵

Submitted to

Department of Biology and Chemistry

生物及化學系

in Partial Fulfillment of the Requirements

for the Degree of Master of Philosophy

哲學碩士學位

by

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April 2008

二零零八年四月

Abstract

In this thesis, the preparation of a number of new ruthenium complexes as potential redox mediators in electrochemical biosensors is reported. These complexes have been characterized by IR, ESI-MS, $^1\text{H-NMR}$, CHN elemental analysis and UV-Vis. Their electrochemical properties have also been investigated.

A series of $[\text{Ru}^{\text{II}}(\text{Me}_3\text{tacn})(\text{acac})(\text{L}^1)]\text{PF}_6$ complexes have been synthesized by the reaction of $[\text{Ru}^{\text{III}}(\text{Me}_3\text{tacn})(\text{acac})(\text{OH})]\text{PF}_6$ with excess L^1 in the presence of Zn/Hg under inert atmosphere. (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane and L^1 = 1-MeIm, 4-Me₂N-py, 4-MeO-py, 4-Me-py, 4-*t*-butyl-py, py, isoquin and 3-Cl-py). Oxidation of these Ru(II) species by $(\text{NH}_4)_2[\text{Ce}^{\text{IV}}(\text{NO}_3)_6]$ in acetone results in the formation of their Ru(III) analogues, isolated as NO_3^- salts. These highly water soluble complexes display one reversible Ru(III)/Ru(II) couple in buffer solution at pH = 8. The $\text{Ru}^{\text{III/II}}$ redox potentials are dependent on L^1 , in the order of 1-MeIm < 4-Me₂N-py < 4-MeO-py < 4-Me-py, 4-*t*-butyl-py < py < isoquin < 3-Cl-py. All complexes have also been characterized by IR, ESI-MS, $^1\text{H-NMR}$, CHN elemental analysis and UV-Vis.

A series of $[\text{Ru}^{\text{II}}(\text{Me}_6\text{tet})(\text{L}^2)]\text{PF}_6$ complexes have been synthesized by the reaction of *cis*- $[\text{Ru}^{\text{III}}(\text{Me}_6\text{tet})\text{Cl}_2]\text{PF}_6$ with various acetylacetonates in the presence of CaCO_3 and Zn/Hg in refluxing ethanol under inert atmosphere (L^2 = acac, Meacac, tfac, bhma, bhba, phpa). Oxidation of these Ru(II) species by $(\text{NH}_4)_2[\text{Ce}^{\text{IV}}(\text{NO}_3)_6]$ in

acetone results in the formation of their Ru(III) analogues, isolated as NO_3^- salts; which can be converted to PF_6^- salts by treatment with NH_4PF_6 in water. The PF_6^- salts of these Ru(III) species can be converted to the Cl^- salts by adding $[\text{Bu}_4\text{N}]\text{Cl}$ to solutions in acetone. These highly water soluble complexes display one reversible Ru(III)/Ru(II) couple in buffer solution at $\text{pH} = 8$. The $\text{Ru}^{\text{III/II}}$ redox potentials are dependent on L^2 , in the order of $\text{Meacac} < \text{phpa} < \text{acac} < \text{bhma} < \text{bhba} < \text{tfac}$. All complexes are also characterized by IR, ESI-MS, $^1\text{H-NMR}$, CHN elemental analysis and UV-Vis.

Treatment of $\text{Ru}^{\text{III}}(\text{acac})_3$ with excess py-3-COOH, py-4-COOH and TMEDA (TMEDA = tetramethylethylenediamine) in refluxing ethanol in the presence of Zn/Hg under argon affords $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{py-3-COOH})_2]$, $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{py-4-COOH})_2]$ and $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{TMEDA})]$ respectively. Air oxidation of these Ru(II) species in aqueous solutions gives $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{py-3-COO})(\text{py-3-COOH})]$, $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{py-4-COO})(\text{py-4-COOH})]$ and $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{TMEDA})]^+$ respectively, isolated as OH^- or PF_6^- salts. These highly water soluble complexes exhibit one reversible couple which is assigned as Ru(III)/Ru(II) couple.

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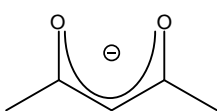
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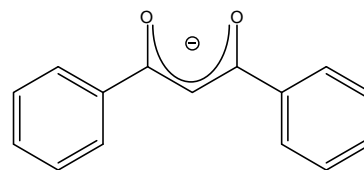
Abbreviations

1-MeIm	1-methylimidazole
3-Cl-py	3-chloropyridine
4-Me-py	4-picoline
4-Me ₂ N-py	4-dimethylaminopyridine
4-MeO-py	4-methoxypyridine
4- <i>t</i> -butyl-py	4- <i>tert</i> -butylpyridine
bpy	2,2'-bipyridine
GOD	glucose oxidase
Hphpy	2-phenylpyridine
Htopy	2-(4'-tolyl)pyridine
isoquin	isoquinoline
Me ₆ tet	<i>N,N,N',N'</i> -tetramethyl-3,6-dimethyl-3,6-diazaoctane-1,8-diamine
NaOAc	sodium acetate
phen	1,10-phenanthroline
pic	picolinate
py	pyridine
py-3-COOH	nicotinic acid
py-4-COOH	isonicotinic acid
pyz	pyrazine
TBHP	<i>tert</i> -butyl hydroperoxide
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine

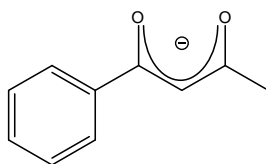
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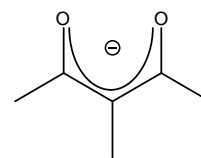
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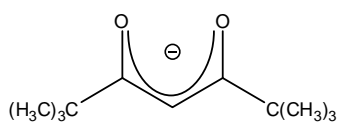
bhma



Meacac



phpa



tfac

