CITY UNIVERSITY OF HONG KONG

香港城市大學

Synthesis and Characterization of Ruthenium Complexes as Redox Mediators of Biosensors

生物傳感器的釕配合物氧化還原媒介的合成及表徵

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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}H-NMR, CHN elemental analysis and UV-Vis. Their electrochemical properties have also been investigated.

A series of $[Ru^{II}(Me_3tacn)(acac)(L^1)]PF_6$ complexes have been synthesized by the reaction of $[Ru^{III}(Me_3tacn)(acac)(OH)]PF_6$ 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-Me_2N-py, 4-MeO-py, 4-Me-py, 4-*t*-butyl-py, py, isoquin and 3-Cl-py). Oxidation of these Ru(II) species by $(NH_4)_2[Ce^{IV}(NO_3)_6]$ 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 $Ru^{III/II}$ redox potentials are dependent on L^1, in the order of 1-MeIm < 4-Me_2N-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}H-NMR, CHN elemental analysis and UV-Vis.

A series of $[Ru^{II}(Me_6tet)(L^2)]PF_6$ complexes have been synthesized by the reaction of *cis*-$[Ru^{III}(Me_6tet)Cl_2]PF_6$ with various acetylacetones 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 $(NH_4)_2[Ce^{IV}(NO_3)_6]$ 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 $[^nBu_4N]Cl$ to solutions in acetone. These highly water soluble complexes display one reversible Ru(III)/Ru(II) couple in buffer solution at pH = 8. The $Ru^{III/II}$ redox potentials are dependent on L^2, in the order of Meacac < phpa < acac < bhma < bhba < tfac. All complexes are also characterized by IR, ESI-MS, ^{1}H-NMR, CHN elemental analysis and UV-Vis.

Treatment of $Ru^{III}(acac)_3$ with excess py-3-COOH, py-4-COOH and TMEDA (TMEDA = tetramethylethylenediamine) in refluxing ethanol in the presence of Zn/Hg under argon affords $[Ru^{II}(acac)_2(py\text{-}3\text{-}COOH)_2]$, $[Ru^{II}(acac)_2(py\text{-}4\text{-}COOH)_2]$ and $[Ru^{II}(acac)_2(TMEDA)]$ respectively. Air oxidation of these Ru(II) species in aqueous solutions gives $[Ru^{III}(acac)_2(py\text{-}3\text{-}COO)(py\text{-}3\text{-}COOH)]$, $[Ru^{III}(acac)_2(py\text{-}4\text{-}COO)(py\text{-}4\text{-}COOH)]$ and $[Ru^{III}(acac)_2(TMEDA)]^+$ 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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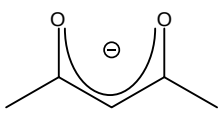
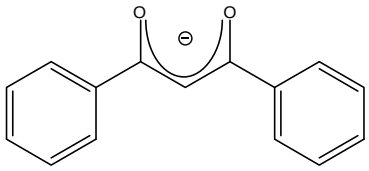
Abbreviations

1-MeIm	1-methylimidazole
3-Cl-py	3-chloropyridine
4-Me-py	4-picoline
4-Me_2N-py	4-dimethylaminopyridine
4-MeO-py	4-methoxypyridine
4-*t*-butyl-py	4-*tert*-butylpyridine
bpy	2,2'-bipyridine
GOD	glucose oxidase
Hphpy	2-phenylpyridine
Htopy	2-(4'-tolyl)pyridine
isoquin	isoquinoline
Me_6tet	*N*,*N*,*N'*,*N'*-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	*tert*-butyl hydroperoxide
TMEDA	*N*,*N*,*N'*,*N'*-tetramethylethylenediamine

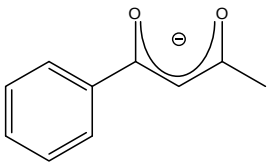
acac



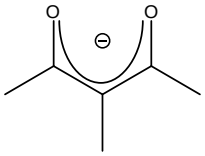
bhba



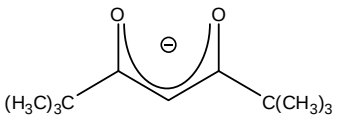
bhma



Meacac



phpa



tfac