

Electrochemical Behavior of Novel Bis (Aliphatic Amine) Ruthenium (II) and Osmium (II) Porphyrins*

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Abstract Bis (aliphatic amine) ruthenium (II) and osmium (II) porphyrins, $M(\text{Por})-(\text{H}_2\text{NR})_2$ and $M(\text{Por})(\text{HNR}')_2$, [$M = \text{Ru}$ and Os ; $\text{Por} = \text{meso-tetrakis}(p\text{-tolyl})\text{porphyrinato}(\text{TTP})$, $\text{meso-tetrakis}(4\text{-chlorophenyl})\text{porphyrinato}(4\text{-Cl-TTP})$, $\text{meso-tetrakis}(3,5\text{-dichlorophenyl})\text{porphyrinato}(3,5\text{-Cl-TTP})$ and $\text{meso-tetraphenyl porphyrinato}(\text{TPP})$; $\text{R} = \text{methyl, ethyl, iso-propyl and } t\text{-butyl}$; $\text{R}' = \text{methyl and ethyl}$] were synthesized by us. The electrochemical behavior of these complexes in 1,2-dichloroethane with TBABF₄ as supporting electrolyte, has been studied by cyclic voltammetry and controlled potential electrolysis. Bis (aliphatic amine) ruthenium (II) porphyrins under go reversible one-electron oxidation and one-electron reduction processes in 1,2-dichloroethane solution. The osmium (II) analogues is shown two oxidation couples III and V, an additional small wave IV. The redox potentials of these complexes are markedly dependent on the nature of the substituent bound to the phenyl group of the porphyrin ring. It is obvious that redox potentials increases the electron-withdrawing power of the substituents increases. The couple I was found at -0.34 , -0.23 and -0.15 V vs $\text{Cp}_2\text{Fe}^{+/0}$ ($\text{Cp}_2\text{Fe} = \text{ferrocene}$) for $\text{Ru}(\text{TPP})(\text{H}_2\text{NBu-t})_2$, $\text{Ru}(4\text{-Cl-TTP})(\text{H}_2\text{NBu-t})_2$ and $\text{Ru}(3,5\text{-Cl-TTP})(\text{H}_2\text{NBu-t})_2$, respectively.

Key words ruthenium osmium porphyrins, cyclic voltammetry, electrochemical behavior

0 Introduction

The electrochemical study of ruthenium porphyrins was first reported by Brown and co-workers in 1973^[1]. It is interesting that the oxidation potentials for $\text{Ru}(\text{TPP})(\text{CO})$ and $\text{Ru}(\text{TPP})(\text{Py})_2$ are markedly different. The carbonyl complexes can be oxidized twice at the ring retaining the metal oxidation state of +2. On the other hand, the bis(pyridine) complex is oxidized first at the metal to +3 state and then at the ring. Evidently, variation of axial ligands causes a shifting of orbitals to make the oxidation of the metal easier in one case. The effect of axial ligands on the redox behavior of ruthenium porphyrins has also been studied by Boschi *et al*^[2]. For the complexes $\text{Ru}(\text{TPP})(\text{L})_2$, where $\text{L} = \text{trialkylphosphine}(\text{PR}_3)$ and isocyanide

($t\text{-BuNC}$), and the carbonyl complex $\text{Ru}(\text{TPP})(\text{CO})$, the potentials related to these processes are strongly dependent on the nature of the axial ligand(L). In fact, ligands with a good π bonding ability, such as CO and $t\text{-BuNC}$, stabilize the porphyrin derivatives in the lower valence state, while making the complexes oxidizable at higher potentials. On the opposite, good σ -donor ligands, such as $\text{P}(\text{Et})_3$, make the derivatives easier to oxidize and then stabilize the anionic complex. In 1981, Rilleman and co-workers reported the influence of the substituent bound to the porphyrin phenyl group on the potentials of ruthenium porphyrins^[3]. Electrochemical studies of osmium porphyrins also appear in the literature [4] and [5]. Herein is described the electrochemical behavior of novel bis(aliphatic amine) ruthenium (II) and osmium (II) porphyrins.

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1 Experimental

1.1 Materials

Bis (aliphatic amine) ruthenium (II) and osmium porphyrin complexes (1 ~ 17) M (Por) (H₂NR')₂ and M(Por)(HNR')₂ were prepared on the methods as described by us^[6]. 1, 2-Dichloroethane was distilled from LiAlH₄. Acetonitrile was stirred with KMnO₄ for 4 h at 25 °C and the mixture refluxed until the liquid was colorless. After removal of the MnO₂ by filtration, the acetonitrile was fractionated from P₂O₅, and the fractionated again from CaH₂ Tetra-n-butyl ammonium fluoroborate (TBABF₄) (electrochemical Grade) was dried at 100 °C under vacuum for 24 h before use. Mercury (GR.) was used as received.

1.2 Apparatus and procedure

Cyclic voltammetry was performed on a Princeton Applied Research (PAR) model 273 A potentiostat and a X-Y recorder. A standard two compartment electrode was used as reference electrode. The working electrode was a glassy carbon disc. All potentials are reported vs the Ag/AgNO₃ electrode. The ferrocenium/ferrocene (Cp₂Fe⁺⁰) couple was used as an internal reference $E_{1/2}$ values are the average of the cathodic and anodic peak po-

tentials for the oxidation and reduction waves. Surface treatments of the glassy carbon electrode involved periodic polishing with *x*-alumina slurry (Linde) on a microcloth followed by rinsing with double distilled water and next sonicating in dichloroethane for 5 min. Solutions for electrochemical studies were deaerated with nitrogen gas, which had been dried by passing through sodium hydroxide and then activated molecular sieve (0.5 nm). Before going into the electrochemical cell, the nitrogen gas was pre-saturated with 1,2-dichloroethane by passing through the pure solvent.

2 Results and discussion

The electrochemical behavior of bis (aliphatic amine) ruthenium (II) and osmium (II) complexes were studied in 1, 2-dichloroethane solution with TBABF₄ as supporting electrolyte by cyclic voltammetry. The $E_{1/2}$ data of these complexes are summarized in Table 1.

It is interesting to compare the redox behavior of Ru (TPP) (Py)₂^[2] and Ru (TPP) (PEt₃)₂^[3], with those of bis (aliphatic amine) ruthenium porphyrins. Since both pyridine and aliphatic amine

Table 1 Redox potential data* of bis (aliphatic amine) ruthenium (II) and Osmium (II) porphyrins

| Complexes | $E_{1/2}/V$ (vs. Cp ₂ Fe ⁺⁰) | | | | |
|--|---|----------|-----------|-----------|----------|
| | couple I | couple I | couple II | couple IV | couple V |
| 1. Ru(TTP)(HNMe ₂) ₂ | -0.33 | 0.82 | | | |
| 2. Ru(TTP)(H ₂ NMe) ₂ | -0.43 | 0.62 | | | |
| 3. Ru(3,5-Cl-TPP)(HNMe ₂) ₂ | -0.15 | 1.07 | | | |
| 4. Ru(TTP)(HNEt ₂) ₂ | -0.35 | 0.83 | | | |
| 5. Ru(4-Cl-TPP)(HNEt ₂) ₂ | -0.24 | 0.93 | | | |
| 6. Ru(TTP)(H ₂ NPr- <i>i</i>) ₂ | -0.40 | 0.71 | | | |
| 7. Ru(4-Cl-TPP)(H ₂ NPr- <i>i</i>) ₂ | -0.25 | 0.83 | | | |
| 8. Ru(TTP)(H ₂ NBu- <i>t</i>) ₂ | -0.34 | 0.76 | | | |
| 9. Ru(4-Cl-TPP)(H ₂ NBu- <i>t</i>) ₂ | -0.23 | 0.85 | | | |
| 10. Ru(3,5-Cl-TPP)(H ₂ NBu- <i>t</i>) ₂ | -0.15 | 0.93 | | | |
| 11. Ru(3,5-Cl-TPP)(HNEt ₂) ₂ | -0.10 | 1.02 | | | |
| 12. Os(TTP)(HNEt ₂) ₂ | | | -0.64 | 0.67 | 0.93 |
| 13. Os(4-Cl-TPP)(HNEt ₂) ₂ | | | -0.55 | 0.72 | 0.98 |
| 14. Os(TTP)(H ₂ NBu- <i>t</i>) ₂ | | | -0.67 | 0.78 | 1.02 |
| 15. Os(4-Cl-TPP)(H ₂ NBu- <i>t</i>) ₂ | | | -0.55 | 0.78 | 1.18 |
| 16. Os(4-Cl-TPP)(H ₂ NPr- <i>i</i>) ₂ | | | -0.57 | 0.91 | 1.18 |
| 17. Os(TTP)(H ₂ NBu- <i>t</i>) ₂ | | | -0.60 | 0.79 | 1.23 |

* potentials were measured at scan rate = 50 mV/s at 25 °C; supporting electrolyte: 0.1 mol/L TBABF₄ in ClCH₂CH₂Cl. The Cp₂Fe⁺⁰ was 0.17 V versus the Ag/AgNO₃ (0.1 mol/L in CH₃CN) reference electrode.

are good σ -donors, their ruthenium(II) porphyrin adducts can be expected to exhibit similar electrochemical behavior. The cyclic voltammogram of Ru(TPP)(Py)₂ showed two oxidations at +0.21 V and +1.26 V vs. ssc in 0.1 mol/L TBAH-CH₂Cl₂ at 25°C^[2]. The first oxidation step (+0.21 V) was assigned to be metal-centered in nature (Ru(II)→Ru(III)), while the second oxidation was assigned to porphyrin ring oxidation (for H₂TPP, at 0.95 V and 1.28 V. vs. ssc in 0.1 mol/L TBAH-CH₂Cl₂ at 25°C). Similar results were also obtained for Ru(TPP)(PEt₃)^[2,3].

By comparison, couple I and II (Fig. 1) can be assigned to the following electrode reactions:

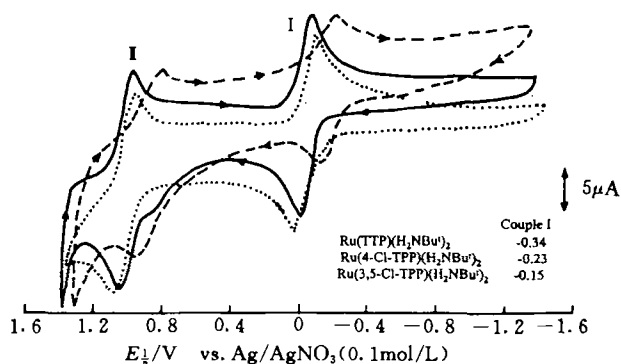
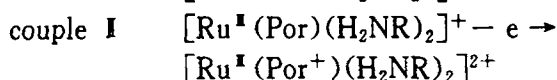
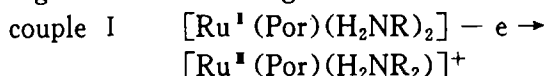
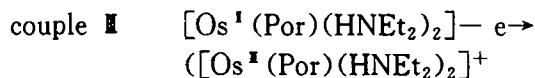


Fig. 1 Cyclic voltammogram of Ruthenium porphyrins

Cyclic voltammogram of Ru(TPP)(H₂NBu^t)₂; ---, Ru(4-Cl-TPP)(H₂NBu^t)₂; —, and Ru(3,5-Cl-TPP)(H₂NBu^t)₂; ···, in ClCH₂CH₂Cl with 0.1 mol/L TBABF₄ as supporting electrolyte (scan rate: 50 mV/s)

It can be seen from Table 1 that the redox potentials of bis(aliphatic amine) ruthenium(II) porphyrins are markedly dependent on the nature of the substituent bound to the phenyl group of the porphyrin ring. For example, couple I was found at -0.34, -0.23 and -0.15 V vs. Cp₂Fe^{+ / o} for Ru(TPP)(H₂Bu-t)₂, Ru(4-Cl-TPP)(H₂NBu-t)₂ and Ru(3,5-Cl-TPP)(H₂NBu-t)₂, respectively (see Fig. 1). Obviously, the redox potentials are shifted anodically as the electron-withdrawing power of the substituent increases, in accord with the substituent sequence found by Rillema and co-workers^[4].

Like the ruthenium(II) analogue the cyclic voltammogram of Os(TTP)(H₂NBu-t)₂ showed two oxidation couple III and V at -0.64 and 0.93 V vs. Cp₂Fe^{+ / o}(Fig. 2). An additional small wave IV appeared at 0.67 V. The E_{1/2} for couple III is more negative than the ruthenium analogue reaction is metal-centered:



The E_{1/2} of couple III for bis(aliphatic amine) osmium(II) porphyrins are also dependent on the nature of the substituents bound to the phenyl group of the porphyrin ring. From Table(1), it is obvious that redox potentials increase as the electron-withdrawing power of the substituents increases.

The oxidation processes at higher potentials (couple IV and V) are quite complex and not totally reversible. They may come from the osmium(III) center,^[5]

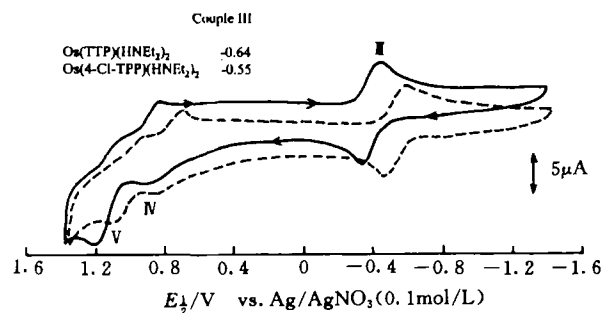
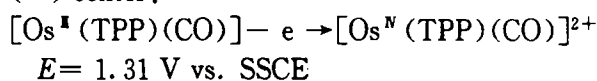


Fig. 2 Cyclic voltammogram of Osmium porphyrins

Cyclic voltammogram of Os(4-Cl-TTP)(HNEt₂)₂; —, and Os(TTP)(HNEt₂)₂; ···, in ClCH₂CH₂Cl with 0.1 mol/L TBABF₄ as supporting electrolyte (scan rate: 50 mV/s)

By comparison with couple II in the ruthenium analogues, couple V in the osmium porphyrins is likely a ligand-centered oxidation, while Mosseri and co-workers assigned the second oxidation of Os(TPP)(CO) to removal of an electron from the osmium(III) center^[5], and couple IV is present in all the diamine osmium porphyrins that we studied. The size and shape of couple IV suggests it is a kinetically sluggish electrode process. Oxidation of the [Os^{III}(Por)-(H₂NR)₂]⁺ or [Os^{III}(Por)-(HNR₂)₂]⁺ may result in the loss of protons from

the amine ligand to form osmium (IV) amino species. The coupling of proton loss with the electron transfer process may cause the electrode reaction to be kinetically slow. Hence couple IV may be assigned as oxidation of the osmium(III) centers to give an osmium(IV) amino intermediate.

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SPECTROSCOPIC STUDY AND APPLICATION ON THE INCLUSION COMPLEXATION OF β -CYCLODEXTRIN WITH ESTRADIOL BENZOATE IN AQUEOUS SOLUTION

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The inclusion complexation reaction of β -cyclodextrin with estradiol benzoate (EB) in the presence of cetyltrimethylammonium bromide has been studied by means of UV absorption and fluorescent spectrometry. The reaction conditions, the formation constant, the mechanism of the host-guest inclusion complex have been studied and a simple, highly sensitive fluorescent synergistic method for the determination of EB has been established with satisfactory results.

Key words β -cyclodextrin, estradiol benzoate, cetyltrimethylammonium bromide, spectral analysis, inclusion complexation