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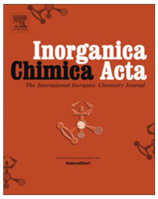

Research paper

Electrochemical behaviour of tris(1,10-phenanthroline)ruthenium(II) at a surface modified electrode. Electrocatalytic reduction of dioxygen

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A R T I C L E I N F O

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A B S T R A C T

Cyclic voltammetry (CV) of $[Ru(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) is studied in CH_3CN under N_2 at a gold electrode whose surface is modified by thiocyanate. Five one-electron ligand reductions are observed on the negative side of normal hydrogen electrode (NHE), which is unprecedented. Using Randles-Sevcik equation, the electrochemical radius of the electrode has been estimated as 0.86 mm (*cf.* physical radius: 1 mm). When the Au-SCN electrode is dipped in an CH_3CN solution of $[Ru(phen)_3]^{2+}$ for 2 h, the cation gets adsorbed on the electrode surface. The resulting Au-SCN-Ru$(phen)_3^{2+}$ electrode shows two reductions in plain CH_3CN under N_2. The number of electrons in each step is found to be 2 when Laviron's equation is applied with a transfer coefficient α of 0.5. Ferrocene at the Au-SCN-Ru$(phen)_3^{2+}$ electrode in CH_3CN shows a one-electron oxidation at 0.681 V vs NHE. The radius of the electrode comes out as 1.02 mm. The heterogeneous rate constant $k_{s,h}$ for the oxidation of ferrocene is found to be 2.77×10^{-2} cm s^{-1} and that at an unmodified Au electrode in CH_3CN 1.03×10^{-2} cm s^{-1}. When CV is performed in CH_3CN in air, the Au-SCN-Ru$(phen)_3^{2+}$ electrode shows electro-catalytic reductions of dioxygen ($O_2 + e \rightarrow O_2^-$ and $O_2^- + e \rightarrow O_2^{2-}$). The $k_{s,h}$ of the first step is found to be 2.99×10^{-3} cm s^{-1} by Nicholson's method (with $\alpha = 0.306$). This $k_{s,h}$ at an unmodified Au electrode is 1.21×10^{-3} cm s^{-1}. In course of the studies, it has been necessary to determine the X-ray crystal structures of $[Ru(phen)_3](NCS)_2$ and $[Ru(phen)_3]_2[Fe(CN)_6]Cl \cdot 18.5H_2O$.

1. Introduction

1,10-Phenanthroline (phen), now known to occur in some marine products, is a versatile ligand in coordination chemistry [1], and $[Ru(phen)_3]^{2+}$ is possibly one of the most studied complexes of phen. The significance of the Ru(II) tris-phen complex and its derivatives in contemporary photochemistry is due to their rich photophysical and electrochemical properties. These complexes can be used as photosensitisers for developing molecular devices, solar cells, photo-catalysts (e.g. water splitting or artificial photosynthesis), and luminescence sensors [2]. They are also of medicinal interest [3]. Earlier we have shown [4–6] how the ancillary neutral N,N donor ligand L determines the nature of the lowest excited state in $[Ru(phen)_2L]^{2+}$ complexes. Thereby we have been able to obtain emissions from ^{3}MC and ^{3}LLCT states, which are rare in the photophysics of Ru(II)N_6 cores. Here our interest is the electrochemical behaviour of the complex cation $[Ru(phen)_3]^{2+}$, the knowledge of which is required to understand its photophysics [5,7]. The working electrode employed here is no ordinary electrode, but a gold electrode whose surface is modified by thiocyanate [8].

2. Results and discussion

It is known that $[Ru(phen)_3](ClO_4)_2$ does not give rise to cyclic voltammograms (CVs) of good quality on the negative side of normal hydrogen electrode (NHE). The situation can be visualized from Fig. 1 where the working electrode is either Pt or glassy carbon. The quality of the voltammogram obtained by Bard and coworkers [9] at a Pt disc microelectrode is somewhat better. Free phen displays two quasi-reversible one-electron reductions around −1.75 and −1.92 V *vs* NHE in dimethylformamide in cyclic voltammetry at a gold disc electrode [10].

A recent observation of one of our laboratories is that use of a gold electrode modified by thiocyanate (Au-SCN) affords much

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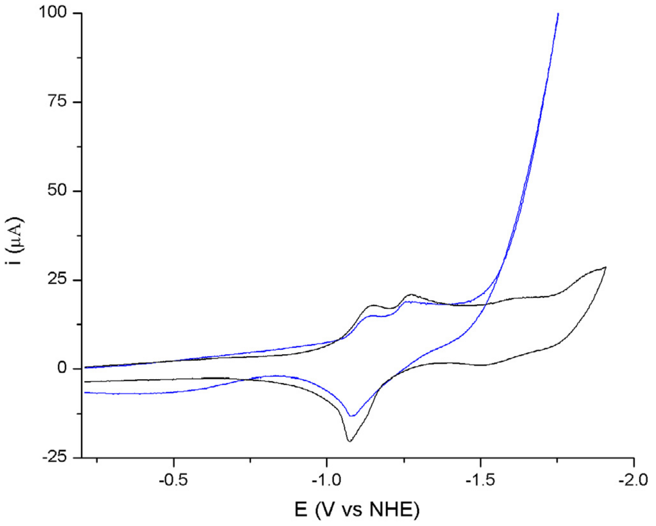

Fig. 1. CVs of $[Ru(phen)_3](ClO_4)_2$ in CH_3CN at a Pt (blue) and a glassy carbon (black) electrode under dry N_2. Supporting electrolyte, 0.1 mol dm^{-3} tetraethyl ammonium perchlorate (TEAP). Solute concentration, 1 mmol dm^{-3}. Scan rate v, 50 mV s^{-1}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

better CVs than a Pt or a glassy carbon electrode in most cases [6,11,12], possibly because the redox active species does not come into direct contact with the electrode material. Accordingly, we have used the Au-SCN electrode to study the cyclic voltammetry of $[Ru(phen)_3](ClO_4)_2$ in acetonitrile on the negative side of NHE. Results are interesting. The peak currents increase with the time of dipping the electrode in the solution of $[Ru(phen)_3](ClO_4)_2$. Initially the forward and the backward traces cross each other. The limiting stage is reached after dipping the Au-SCN electrode in the acetonitrile solution for 1.5 h (Fig. 2; see also Fig. S1 of supplementary material).

The cyclic voltammetric response obtained above is diffusion controlled as the cathodic peak current (i_{pc}) of the first wave in Fig. 2 with an apparent redox potential $E_{1/2}$ of −0.65 V *vs* NHE is found to be proportional to $v^{1/2}$ (Fig. 3). Consequently, the Randles-Sevcik equation [13], Eq. (1)

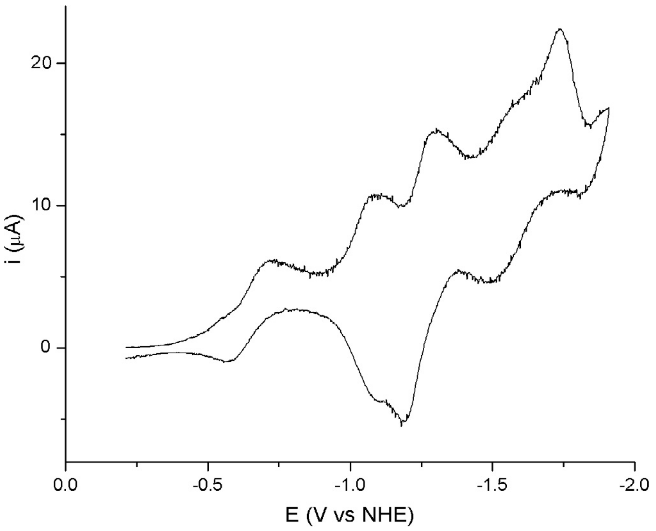

Fig. 2. CV of $[Ru(phen)_3](ClO_4)_2$ in CH_3CN after dipping the Au-SCN electrode for 1.5 h in the solution under dry N_2 atmosphere. Solute concentration, 1 mmol dm^{-3}; supporting electrolyte, 0.1 mol dm^{-3} TEAP; v, 50 mV s^{-1}.

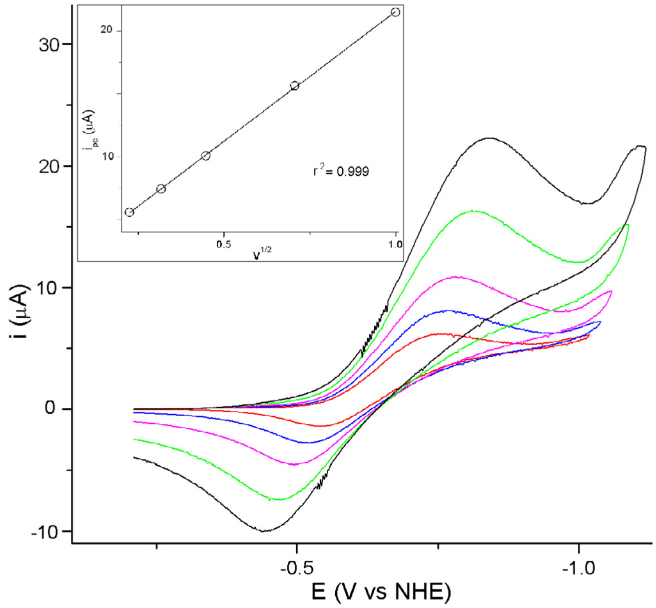

Fig. 3. Cyclic voltammetric response with $E_{1/2}$ = −0.65 V *vs* NHE obtained in Fig. 2 at various scan rates v (red, 0.05; blue, 0.10; purple, 0.20; green, 0.50; black, 1.00 V s^{-1}). The inset is a plot of i_{pc} with $v^{1/2}$ (the intercept of 0.43 ± 0.10 μA is neglected). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$i_{pc} = 2.69 \times 10^5 D_O^{1/2} n^{3/2} C_O A v^{1/2} \qquad (1)$$

holds. Here i_{pc} is expressed in amp, v in V s^{-1}, the area A of the electrode in cm^2, the bulk concentration C_O of the oxidized species in mol cm^{-3} and diffusion coefficient D_O of the oxidized species in $cm^2\ s^{-1}$. Finally, n in Eq. (1) is the number of electrons involved in the redox process.

Actually Eq. (1) is meant for a reversible electron transfer. Judging by the peak-to-peak separation ΔE_p, all the responses in Fig. 2 show a lack of reversibility (for a reversible process ΔE_p should be strictly 57 mV together with the ratio i_{pc}/i_{pa} of cathodic and anodic peak currents = 1). Considering linear diffusion, increase in i_{pc} with time t (Fig. 4) seems to be directly related to the fractional coverage (θ) of the surface of the negatively charged electrode by the $[Ru(phen)_3]^{2+}$ cation. θ is equal to i_{pc}/i_{max} and the i_{max} in our case is 5.71 μA (Fig. 2). The inset in Fig. 4 shows that θ increases linearly with time, i.e. the process of weak physical adsorption of the ruthenium cation on the Au-SCN surface follows the kinetics of a zero order reaction. As Fick's law holds here, it can be assumed that the adsorption is weak. Such situations are known in protein electrochemistry [13]. Later we shall encounter a situation where the adsorption is strong and non-Fickian effects are observed.

To check whether the results are in order, we have tried to estimate the area A of the electrode surface at the limiting condition from the i_{pc} in Fig. 2 by using Eq. (1) with the experimental diffusion coefficient of $[Ru(phen)_3]^{2+}$ in acetonitrile [14] as $16.5 \times 10^{-6}\ cm^2\ s^{-1}$. The electrochemical radius of the electrode is found to be 0.86 mm. This matches well with the physical radius of the unmodified PAR Au milli electrode of 1 mm. It has previously been mentioned that for accurate determination of the area of an electrode chronoamperometry is recommended [15].

Like 2,2′-bipyridine (bpy), phen is an α-diimine. Tris-α-diimine complexes should ideally display six ligand based reductions – two per α-diimine moiety [16–18]. Usually these are transferred in two sets of three electrons forming a redox series. The number of electrons transferred in a step seems to depend on the type of electrode. While at an ordinary Pt disc electrode six one-electron