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Formation and oxidative break-up of organometallic Ru–Ru bonded polymer films in DMSO electrolyte studied using the dimer $[Ru(bpy)(CO)_2Cl]_2$ (bpy = 2,2′-bipyridine)

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ABSTRACT

The dimer $[Ru(bpy)(CO)_2Cl]_2$ dissociates in DMSO electrolyte to form free chloride and DMSO-coordinated monocation with an equilibrium constant of ca. 6×10^{-4} mol dm^{-3}. Neutral dimer is oxidised with peak potential $E_p = +0.75$ V (vs. Ag/AgCl, $c_{KCl} = 3.4$ mol dm^{-3}) in a one-electron process. The monocation (reduced in one-electron process with $E_p = -0.96$ V) is able to reversibly dissociate into dicationic dimer, reduced with $E_p = -0.85$ V. Mostly monocationic tetramer is formed during electrolysis at -1 V which in turn is reduced to form monocationic octamer with $E_p = -1.09$ V. EQCM, RRDE and voltammetric data indicate that reduction of the octamer results in hexadecamer formation and deposition in a process with $E_p = -1.14$ V. A model for the reduction voltammetry was tested using digital simulation. UV–vis and voltammetric results show that tetramers are formed in the oxidative break-up of the Ru–Ru bonded film. These tetramers can be oxidised back to dimers in two one-electron processes via a stable intermediate. Such dimers can be back-reduced to form film.

1. Introduction

Nonbridged metal–metal bonded polymers formed by electroreduction of monomeric or dimeric organometallic Ru(bpy) or Os(bpy) complexes [1–11] constitute a unique group of materials possessing promising catalytic and conducting properties. The established electrocatalytic activity of these materials in CO_2 reduction [6,9,12–14] is of great technical interest, especially after improvement of the air-sensitivity of the material following suspension of the catalyst precursor on a supporting polymer network [13,14]. Also the conducting capability is interesting from a molecular electronics point of view [15]. Namely, the known partial oxidation process involving the metal centres in the Ru^0–Ru^0 chain [6,14], the short Ru–Ru bond length and the proposed structure [16] makes the material similar to well conducting, partially oxidised chains formed by stacking of e.g. square-planar Pt [17] or Ir [18] d^8 complexes. We have also recently found that the film conductance increases following partial oxidation [19].

Coulometric [1–4,6,13] as well as rotating disc electrode (RDE) and electrochemical quartz crystal microbalance (EQCM) results [8] show that electropolymerisation of the monomer $Ru^{II}(bpy)(CO)_2Cl_2$ in CH_3CN electrolyte is rapid and quantitative. In contrast, in DMSO electrolyte, the electroreduction/deposition processes using this monomer are clearly altered as a result of strong Ru^I–DMSO interaction, which causes chloride decoordination from intermediates [20]. One such was identified as a soluble cationic dimer and indications were that even longer soluble fragments were present. Thus, it seems clear that DMSO is able to coordinate to the Ru^I end-groups of oligomers but detailed information on the influence this has on electropolymerisation is lacking. In this context we report here on voltammetric, EQCM and spectrophotometric results obtained for the chemically synthesized dimer ((a) in Fig. 1) in DMSO, both regarding the reductive film formation process and the oxidative film stripping processes.

2. Experimental

Materials and chemicals used, as well as the instrumentation and experimental procedures, have been described elsewhere [8,20]. Dimethyl formamide (DMF), Lab-Scan A.R., was used as received. Dimer dissolution and dissociation equilibrium was reached in ca. 30 min after addition of solid dimer to DMSO electrolyte. This was concluded from attainment of constant chloride oxidation signal and UV–vis absorbance after this time. Thus, a waiting period of 30 min was used before making measurements. Ag/AgCl ($c_{KCl} = 1$ and 3.4 mol dm^{-3}) reference electrodes were used. All potential values given here are vs. the latter. EQCM measurements were made with a Seiko EG&G Model QCA917 quartz

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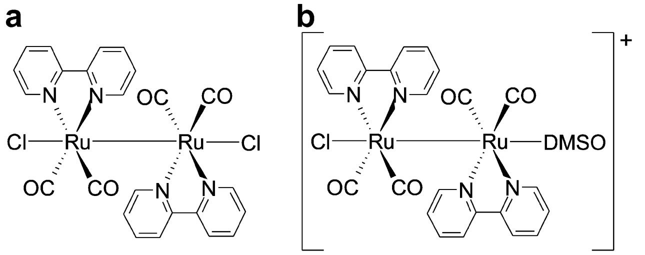

Fig. 1. Schematic molecular structures of (a) *trans*(Cl)-$[\mathrm{Ru(bpy)(CO)_2Cl}]_2$ dimer and (b) its monocationic form formed after decoordination of chlorido ligand.

crystal analyser using Au-coated 10 MHz AT-cut quartz crystal discs, with an oscillating area of 0.21 cm^2. Bulk electrolysis charges were corrected by subtracting background charges obtained in pure electrolyte. IR spectra were recorded in a 0.1 mm thin layer cell with KBr windows using a Nicolet Nexus 870 FTIR spectrometer (1024 scans, 4 cm^{-1} resolution). Solutions were transferred from a two compartment electrolysis cell using an oxygen tight quartz capillary tube. Digital simulations were made using the DigiElch 3 program (ElchSoft, Kleinromstedt, Germany).

3. Results and discussion

3.1. Dimer dissociation equilibrium in DMSO

The dimer dissociates to form ions when dissolved in DMSO. This process causes the appearance of free chloride in DMSO-based electrolyte solution [20]. Likewise, when the dimer was dissolved in pure DMSO, the electric conductivity of the solution increased with the same time dependence as the chloride concentration in the electrolytic solutions. It is proposed that the dissociation of chloride is reversible according to Eq. (1):

$$[\mathrm{Ru^I(bpy)(CO)_2Cl}]_2 + \mathrm{DMSO} \overset{k_1}{\leftrightarrow} [\{\mathrm{Ru^I(bpy)(CO)_2}\}_2\mathrm{Cl(DMSO)}]^+ + \mathrm{Cl^-}. \tag{1}$$

An equilibrium constant, k_1, for this reaction can be written

$$k_1 = \frac{\left[\left[\{\mathrm{Ru^I(bpy)(CO)_2}\}_2\mathrm{Cl(DMSO)}\right]^+\right][\mathrm{Cl^-}]}{\left[\left[\mathrm{Ru^I(bpy)(CO)_2Cl}\right]_2\right]} \tag{2}$$

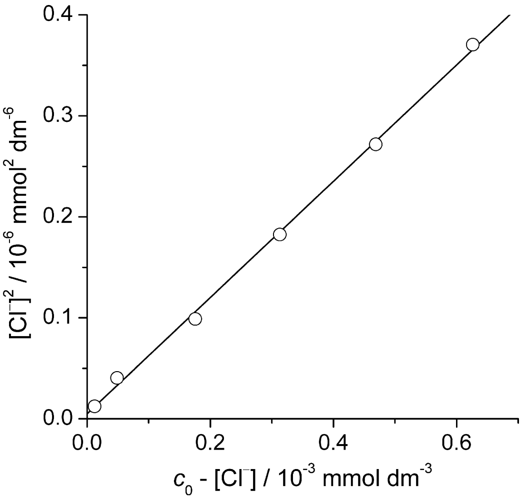

Fig. 2. Plot of $[\mathrm{Cl^-}]^2$ against c_0–$[\mathrm{Cl^-}]$ for total $[\mathrm{Ru(bpy)(CO)_2Cl}]_2$ concentration c_0 = 0.12, 0.25, 0.49, 0.74, 0.99 and 1.23 mmol dm^{-3}.

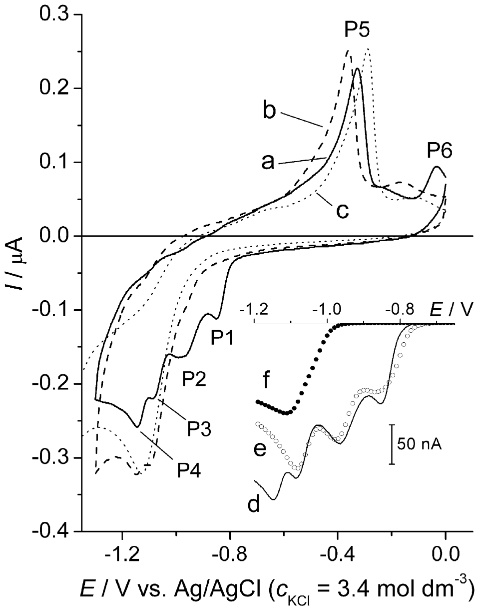

Fig. 3. Typical CV responses (2nd cycle) for: (a) $[\mathrm{Ru(bpy)(CO)_2Cl}]_2$ in DMSO electrolyte (c_0 = 0.28 mmol dm^{-3}), (b) previous system after addition of LiCl ($c_{\mathrm{LiCl}} \approx 45$ mmol dm^{-3}), and (c) $[\mathrm{Ru(bpy)(CO)_2Cl}]_2$ in DMF electrolyte (c_0 = 0.31 mmol dm^{-3}), with current multiplied by 0.435. Sweep rate v = 50 mV s^{-1}. P1–P6 indicates processes discussed in text. Inset shows initial negative sweep for $[\mathrm{Ru(bpy)(CO)_2Cl}]_2$ (d), simulations of (d) without (e) and in presence of (f) LiCl (c_{LiCl} = 45 mmol dm^{-3}).

and knowledge about the dependence of $[\mathrm{Cl^-}]$ on the total dimer concentration, c_0, can be used to estimate its value. A voltammetric oxidation signal (that of P9 in Fig. 4) can be used for quantification of Cl$^-$, but the signal is depressed when dimer is present in higher concentrations ($c_0 > 1.5$ mmol dm^{-3}), which makes chloride quantification unreliable for these. For lower c_0 the oxidation signal is proportional to $[\mathrm{Cl^-}]$ and quantification more reliable (as found by addition of LiCl to low c_0 solution). Fig. 2 shows such voltammetrically obtained data in the form of $[\mathrm{Cl^-}]^2$ plotted against c_0–$[\mathrm{Cl^-}]$. The plot has a linear appearance and the value of k_1 provided by the slope of the linear regression line is 5.8×10^{-4} mol dm^{-3}. The electrochemistry of dimer in DMSO deviates from that in DMF for instance, which is unable to spontaneously replace axial chlorido ligand, and the unusual features can to a large extent be explained by assuming the existence of equilibria similar to that of Eq. (1), involving a number of Ru$^{\mathrm{I}}$-species and chloride. Accordingly, it will be demonstrated below that also the second chlorido ligand of the dimer in DMSO dissociates, but to a much lower extent. For the analogous $\mathrm{CH_3CN}$-coordinated dicationic dimer in $\mathrm{CH_3CN}$ a 3:1 chloride-to-dimer ratio is sufficient for quantitative transformation of it into dichloride dimer [7]. By assuming 99% transformation and by using the experimental dimer concentration given (1 mmol dm^{-3}) a chloride dissociation constant of ca. 10^{-5} mol dm^{-3} is obtained in this system. Thus, chloride is apparently more easily replaced by solvent in DMSO than in $\mathrm{CH_3CN}$. The resulting low solubility of the current chloride-coordinated dimer in $\mathrm{CH_3CN}$ makes reliable measurements difficult in such a system.

3.2. Overall voltammetry of dimer in DMSO

The solid line in Fig. 3 shows a typical CV cycle obtained for equilibrated dimer solution with a negative potential limit of −1.3 V. Six processes marked P1–P6 are clearly visible in the voltammogram with corresponding peak potentials $E_{\mathrm{p1}} = -0.85$ V,