Electrochemistry of $[\{Ru^{III}L_2(OH_2)\}_2O]^{4+}$ complexes in a non-coordinating solvent (L = substituted 2,2′-bipyridine): application to the elaboration of corresponding functionalized polypyrrole films

Marie-Noëlle Collomb Dunand-Sauthier, Alain Deronzier* and Marcelo Navarro

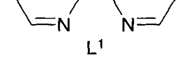
Laboratoire d'Electrochimie Organique et de Photochimie Rédox, Université Joseph Fourier-UMR CNRS 5630, BP 53, 38041 Grenoble Cédex 9, France

$[\{Ru^{III}L_2(OH_2)\}_2O]^{4+}$ complexes are synthesized (L = substituted 2,2′-bipyridine) and studied in a non-coordinating CH_2Cl_2 electrolyte in order to elaborate by electropolymerization corresponding polypyrrole functionalized films.

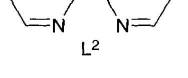
The ruthenium μ-oxo dimer *cis*-$[\{Ru^{III,III}(bpy)_2(OH_2)\}_2O]^{4+}$ **1** (bpy = 2,2′-bipyridine), is a remarkable catalyst for the oxidation of water,[1] chloride ion[2] or organic compounds.[3] The oxidation chemistry is based on the formation of the higher oxidation state oxo complex which is obtained by a series of electron–proton loss steps from the aquo complex **1**. Only rare examples of immobilization of such catalysts on electrode surfaces have been reported, all attempts are based on the incorporation of complex **1** by cation exchange into thin polymeric films of partially hydrolysed *p*-chlorosulfonated polystyrene,[4] on Nafion®,[5] or on its immobilization in a carbon paste.[6] These devices are reputed to have rather poor stability due to the leaching of the complex from the film.[4]

We have previously reported an example of modified electrodes containing this complex based on an electropolymerization technique in which this disadvantage is suppressed.[7] $[Ru(bpy)_2Cl_2]$ sites immobilized *via* a functionalized polypyrrole film have been chemically converted *in situ* into $[\{Ru^{III}(bpy)_2(OH_2)\}_2O]^{4+}$ sites. We show here a more straightforward strategy to elaborate by electropolymerization similar modified electrodes. For this purpose, the new complex $[\{Ru^{III}(L^1)_2(OH_2)\}_2O]^{4+}$ **2** has been synthesized[8] [L^1 = 4-(4-pyrrol-1-ylbutyl)-4′-methyl-2,2′-bipyridine] from the aquo complex $[Ru^{II}(L^1)_2(OH_2)_2]^{2+}$ **3** precursor. **1** is known to undergo aquo ligand substitution by solvents such as MeCN.[9] Since complex **1** is not soluble in non-coordinating solvents such as CH_2Cl_2, we first investigated the electroactivity of another unpolymerizable model complex, $[\{Ru^{III}(L^2)_2(OH_2)\}_2O]^{4+}$ **4** (L^2 = 4,4′-di-*tert*-butyl-2,2′-bipyridine) in this medium. This new complex **4** was prepared *in situ* from a CH_2Cl_2 solution of *cis*-$[Ru^{II}(L^2)_2(OH_2)_2]^{2+}$ **5** or by a chemical route.[8]

When a red–brown solution of *cis*-diaquo ruthenium(II) complex **5** in CH_2Cl_2 is saturated with oxygen and stirred for a few hours at room temperature, an intense blue–green solution results. A similar phenomenon has been previously reported[10] for some ruthenium(II) complexes, *e.g.* $[Ru(bpy)_2Cl(Me_2CO)]^+$ in acetone solutions, and attributed to the quantitative formation of μ-oxo dimeric species. The absorption spectra recorded during the oxidation reaction of **5** (Fig. 1) show that the peaks at 335 and 476 nm decrease along with an increase in absorbance at 650 nm assigned to the formation of the dimeric complex **4**. After the band at 650 nm has reached its maximum intensity, the cyclic voltammogram of this solution in the presence of NBu_4BF_4 (0.1 mol dm^{-3}) shows a reversible wave at $E_{1/2}$ = 0.98 V *vs.* SCE (Fig. 2) which corresponds to the one-electron oxidation of the $Ru^{III}Ru^{III}$ dimer to give the $Ru^{III}Ru^{IV}$ species $[(OH_2)L^2{}_2Ru^{III}ORu^{IV}L^2{}_2(OH)]^{4+}$ **6**. Also, exhaustive oxidation of **4** at 1.25 V consumes one electron per molecule and furnishes a solution with an absorption band at 454 nm (Fig. 2). This absorption spectrum is similar to that obtained for



L^1



L^2

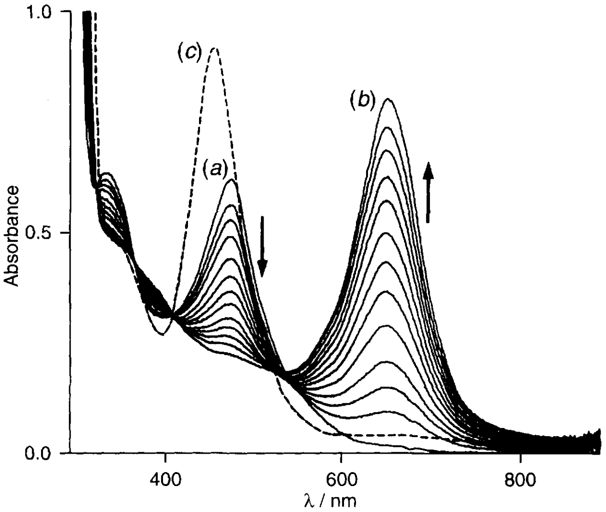


Fig. 1 Changes in the absorption spectra during oxidation with oxygen of a solution of **5** (0.7 × 10^{-3} mol dm^{-3}) in CH_2Cl_2. Formation of **4**: (*a*) 0 s, (*b*) 3 h, (*c*) after oxidation at 1.25 V in NBu_4BF_4–CH_2Cl_2.

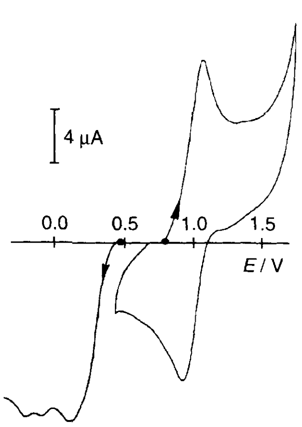


Fig. 2 Cyclic voltammogram of **4** in NBu_4BF_4–CH_2Cl_2 (0.1 mol dm^{-3}), formed according to Fig. 1 at a glassy carbon electrode (diameter 5 mm); v = 50 mV s^{-1}

6 in acidic aqueous solution.[11] In contrast to what is observed in acidic aqueous solution, no further waves corresponding to the formation of higher oxidation states (*e.g.* $Ru^{IV}Ru^{IV}$) species are clearly detected. This difference is due to the slower associated proton transfer in CH_2Cl_2.[12] The successive irreversible reduction waves located at 0.10, −0.10 and −0.22 V observed on the cyclic voltammogram of **4** correspond to the reduction of the complex associated with the decomposition of the dimeric structure yielding $[Ru^{II}(L^2)_2(OH_2)(BF_4)]^{+}$[13] and other unidentified mononuclear ruthenium(II) species.

An authentic sample of the dimer **4**, synthesized from **5**[13] using the biphasic medium H_2O–CH_2Cl_2 in the presence of 1% $AgBF_4$, exhibits absorbance and electrochemical properties identical with those of the sample obtained upon oxygen oxidation in CH_2Cl_2.

The μ-oxo dimer **2** cannot be prepared *in situ* in CH_2Cl_2 by oxygen oxidation. The saturation with oxygen of a solution of the *cis*-diaquo ruthenium(II) complex **3** in CH_2Cl_2 induced the rapid polymerization of the complex attested by the formation of a dark precipitate in solution. Compound **2** has been prepared and isolated as compound **4** and exhibits the same basic electrochemical behaviour in CH_2Cl_2. For a fresh solution of **2** on the first scan the expected $Ru^{III}Ru^{III}$–$Ru^{III}Ru^{IV}$ reversible system is detected at $E_{1/2}$ = 0.96 V, followed by the irreversible oxidation of the pyrrole group (E_{pc} = 1.22 V, not shown). Modified electrodes by poly-**2** films can be obtained on platinum or glassy carbon electrodes by successive scans from 0.60 to 1.20 V at $v = 50$ mV s^{-1}. Fig. 3(*a*) shows the continuous increase in the size of the cyclic voltammogram peaks for the $Ru^{III}Ru^{III}$–$Ru^{III}Ru^{IV}$ couple during the growth of a poly-$[\{Ru^{III}(L^1)_2(OH_2)\}_2O]^{4+}$ film at a glassy carbon electrode. The steady growth of the film indicates an excellent efficiency of the electropolymerization process. The potential range is restricted to 0.60 V to avoid irreversible reduction of the dimer during its formation. Polypyrrole electroactivity is not detected owing to the very positive potential used for its fabrication; its electroactivity is destroyed as it is formed as a consequence of the fast overoxidation of polypyrrole at the potential applied.[14] These modified electrodes (*e.g.* $\Gamma = 3.5 \times 10^{-8}$ mol cm^{-2}), when transferred to pure NBu_4BF_4–CH_2Cl_2 solution and scanned between 0.70 and 1.40 V, show the typical reversible $Ru^{III}Ru^{III}$–$Ru^{III}Ru^{IV}$ couple which lies at a potential ($E_{1/2}$ = 1.0 V) close to that of **4** in solution [Fig. 3(*b*)]. Although no clear reduction peak appears in the cathodic area, cycling the poly-**2** films between 0.0 and 1.20 V induces a slow breakdown of the dimeric structure as for **4**.

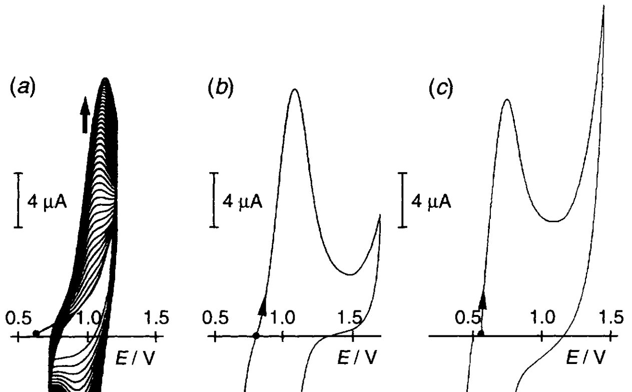


Fig. 3 (*a*) Oxidative electropolymerization by successive scans at a glassy carbon electrode (diameter 3 mm) of **2** (0.5×10^{-3} mol dm^{-3}) in NBu_4BF_4–CH_2Cl_2 (0.1 mol dm^{-3}); (*b*) and (*c*), cyclic voltammograms of a similar modified electrode ($\Gamma = 3.5 \times 10^{-8}$ mol cm^{-2}) upon transfer to clean CH_2Cl_2 electrolyte and to $HClO_4$–H_2O (0.1 mol dm^{-3}) respectively; $v = 50$ mV s^{-1}

Fig. 3(*c*) shows the cyclic voltammogram of the same modified electrode in acidic aqueous solution (0.1 mol dm^{-3} $HClO_4$). In this medium the electrochemical response of the film is similar to those previously reported for modified electrodes obtained from a chemical transformation of a poly$[Ru(L^1)_2Cl_2]$ film.[7] When scanned between 0.40 and 1.40 V, only the well defined wave due to the proton-coupled one-electron oxidation of the dimer[4] is observed ($E_{1/2}$ = 0.68 V *vs.* SCE). Waves for higher oxidation states do not appear for the film as a consequence of kinetic effects.[12,15] The stability of the films was investigated by continuously cycling the potential. After 30 successive scans between 0.50 and 1.0 V, a steady state is reached and only 8% of the complex activity is lost. The electrochemical reductive cleavage of the dimer $[\{Ru^{III}(L^2)_2(OH_2)\}_2O]^{4+}$ into *cis*-$[Ru^{II}(L^1)_2(OH_2)_2]^{2+}$ can be achieved by maintaining the electrode potential at −0.20 V over 90 min. The initial reversible system at $E_{1/2}$ = 0.68 V is replaced by a new one at $E_{1/2}$ = 0.60 V[13] typical of the Ru^{II}–Ru^{III} peak system of the monomeric complex.

Films of poly-**2** can also readily be deposited on an optically transparent electrode (ITO). Here the electropolymerization was accomplished at a constant potential of 1.05 V. Films, reduced back at 0.70 V to restore the $Ru^{III}Ru^{III}$ form of the complex prior to analysis, exhibits the typical absorption band at 654 nm of the dimeric structure.

Further studies concerning the electrocatalytic properties of the new species are now currently under investigation.

We are grateful to Dr H. Le Bozec for a gift of ligand L^2. M. N. thanks CNPq, (Consehlo Nacional de Presquisae Desenvolvimento Technologica, Brazil) for financial support.

References

1 Y. Lei and J. K. Hurst, *Inorg. Chem.*, 1994, **33**, 4460 and references therein.
2 C. D. Ellis, J. A. Gilbert, W. R. Murphy Jr. and T. J. Meyer, *J. Am. Chem. Soc.*, 1983, **105**, 4842.
3 W. Kutner, J. A. Gilbert, A. Tomaszewski, T. J. Meyer and R. W. Murray, *J. Electroanal. Chem.*, 1986, **205**, 185; A. Gerli and J. Reedijk, *J. Mol. Catal.*, 1994, **89**, 101; S. J. Raven and T. J. Meyer, *Inorg. Chem.*, 1988, **27**, 4478.
4 W. J. Vining and T.J. Meyer, *Inorg. Chem.*, 1986, **25**, 2023.
5 R. Ramaraj, A. Kira and M. Kaneko, *Polym. Adv. Technol.*, 1995, **6**, 131.
6 W. Kutner, *J. Electroanal. Chem.*, 1989, **259**, 99.
7 W. F. De Giovani and A. Deronzier, *J. Chem. Soc., Chem. Commun.*, 1992, 1461.
8 M.-N. Collomb Dunard-Sauthier, A. Deronzier and M. Navarro, manuscript in preparation.
9 J. C. Dobson, B. P. Sullivan, P. Doppelt and T. J. Meyer, *Inorg. Chem.*, 1988, **27**, 3863.
10 T. R. Weaver, T. J. Meyer, S. A. Adeyemi, G. M. Brown, R. P. Eckberg, W. E. Hatfield, E. C. Johnson, R. W. Murray and D. Unterecker, *J. Am. Chem. Soc.*, 1975, **97**, 3039.
11 J. A. Gilbert, D. S. Eggleston, W. R. Murphy Jr., D. A. Geselowitz, S. W. Gersten, D. J. Hodgson and T. J. Meyer, *J. Am. Chem. Soc.*, 1985, **107**, 3855.
12 W. F. De Giovani and A. Deronzier, *J. Electroanal. Chem.*, 1992, **337**, 285.
13 M.-N. Collomb Dunand-Sauthier, A. Deronzier, H. Le Bozec and M. Navarro, *J. Electroanal. Chem.*, 1996, **410**, 21.
14 A. Deronzier and J.-C. Moutet, *Curr. Top. Electrochem.*, 1994, **3**, 159; *Coord. Chem. Rev.*, 1996, **147**, 339.
15 A. R. Guadalupe, X. Chen, B. P. Sullivan and T. J. Meyer, *Inorg. Chem.*, 1993, **32**, 5502.

Received, 29th April 1996; Com. 6/02961B