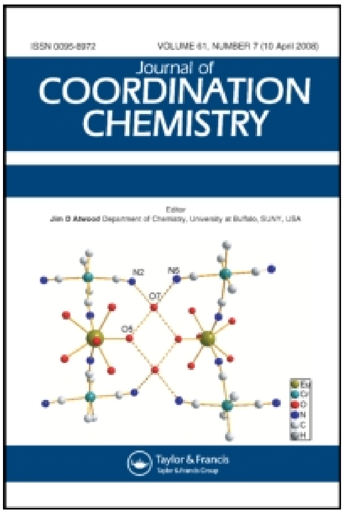

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SYNTHESIS, PROPERTIES AND AN ELECTROACTIVE FILM OF RUTHENIUM(II) COMPLEXES WITH THE PYRIDINE DERIVATIVE LIGAND: *trans*-[$RuCl_2(pmp)_4$].(pmp=3-(PYRROL-1-YLMETHYL)PYRIDINE)

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SYNTHESIS, PROPERTIES AND AN ELECTROACTIVE FILM OF RUTHENIUM(II) COMPLEXES WITH THE PYRIDINE DERIVATIVE LIGAND: *trans*–$[RuCl_2(pmp)_4]$.(pmp=3-(PYRROL-1-YLMETHYL)PYRIDINE)

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In this work we report the synthesis, characterization and electrochemistry of the complex *trans*-$[RuCl_2(pmp)_4]$, where pmp=3-(pyrrol-l-ylmethyl)pyridine. The complex was characterize by electronic spectroscopy (λ_{max} = 404 nm and ε = 27000), vibrational FT-IR spectroscopy, ^1H and ^{13}C NMR, showing results typically in agreement with *trans* geometry. Cyclic voltammetry reveals a redox process centered on the Ru(II) center ($E^{1/2}$ = 0.53V *vs.* NHE), which is electrochemically and chemically reversible. Spectroelectrochemistry shows the progressive disappearance of bands at 404 and 475 nm and the appearance of a new band at 302 nm during the oxidation process. Cyclic voltammetric experiments were performed to characterize the redox properties of the ruthenium complex; its electropolymerization produced a strongly adhesive conducting polymeric film on platinum and palladium electrodes.

Keywords: ruthenium(II); 3-(pyrrol-l-ylmethyl)pyridine; electropolymerization; redox polymer; spectroelectrochemistry; modified electrodes

INTRODUCTION

Coordination compounds of general formula *trans*-$[RuX_2(L)_4]$ (where X=Cl, Br, I; L = monodentate ligand) are widely known in the literature, and several complexes having pyridine and its derivatives have been prepared and characterized.[1–4] The increasing interest in these compounds is due to the interesting properties and the possibility of applications in practical situations. For instance, the compound *trans*-

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[$RuCl_2(dmso)_4$] (dmso = dimethyl sulfoxide) shows promising results in tests of antitumor activities.[5] In addition, such compounds might be used as starting materials in the preparation of six coordinate ruthenium tetra(pyridine) nitrosyl complexes[6] and ruthenium (IV) compounds with axial oxide,[7] *trans*–[$RuX(O)(L)_4$]$^+$. The use of this complex in catalytic systems is very promising. One additional advantage of the system is the possibility of using the ligand L according to specific needs. In this work, the ligand pmp (pmp=3-(pyrrol-l-ylmethyl)pyridine) was chosen for the possibility of undergoing electropolymerization *via* the pyrrole moiety, allowing the complex *trans*–[$RuCl_2$ ($pmp)_4$] to act as a redox center on an inert electrode surface. It is well known that polypyrrolic films are widely applied in modified electrodes for electrocatalysis, biossensors and electrochromic devices.[8–10] Early studies involving N–substituted pyrrole show a correlation between the features of the formed films and the substituent groups attached through the nitrogen ring.[8] The addition of a pyrrolic monomeric unit in the electrochemical solution leads to formation of a copolymer and subsequent improvement in the general properties of the formed film.[11] Electropolymerization is also improved by use of monomers with more than one pyrrole moiety connected to the active redox group.[8] There is a strict correlation with the number of pyrrolic units attached to the metal center and the efficiency of the film forming copolymers. In this article, we report the results of the synthesis, characterization and preliminary electrochemistry of *trans*-[$RuCl_2(pmp)_4$], as illustrated in Figure 1. The main goal is the synthesis of a ruthenium complex with four pyrrolic substituents attached to the pyridine ligands, to achieve better electropolymerization. According to Pickup and Ochmanska[11] steric hindrance often prevents the polymerization of species with just one pyrrole group.

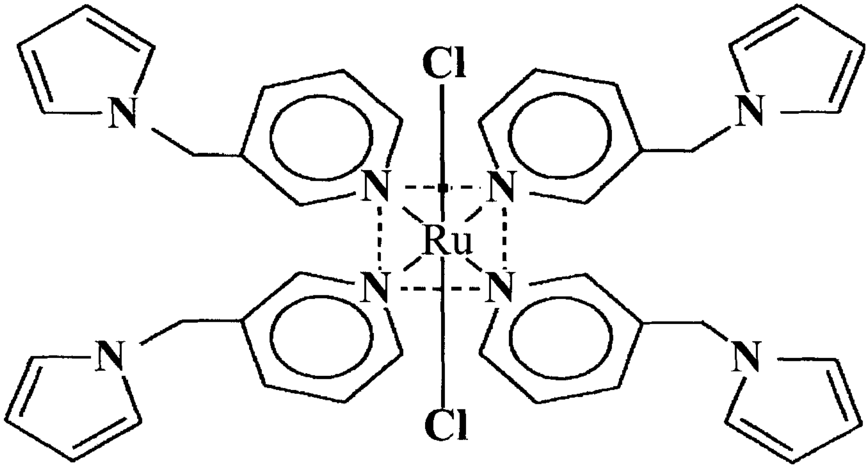

FIGURE 1 Proposed strucuture for *trans*-[$RuCl_2(pmp)_4$].

This led us[18–19] to synthesise coordination complexes with four pyrrole substituents. Another approach is the technique of co-polymerization of a ruthenium complex with the readily polymerizable unsubstituted pyrrole. Recently, we sythesized and characterized[18] a tetranuclear copper(I) complex containing four pyrrolic substituents attached to the pyridine ligand, which had promising result[19] as copolymer in electropolymerization.

EXPERIMENTAL

Reagents

All reagents and solvents employed in this work were of analytical grade and were purchased from several commercial sources. $RuCl_3{\cdot}3H_2O$ (Jonhson–Matthey) and 3-(pyrrol-1-ylmethyl)pyridine (Aldrich) were used without further purification. The supporting electrolyte, tetrabutylammonium hexafluorphosphate (HTBA-Aldrich), was dissolved in warm acetone and precipitated with addition of ultrapure water. The solid was dried under high vacuum for 24 h. The solvents employed in electronic spectroscopy were spectroscopic grade reagents and were used without further purification. In electrochemical and spectroelectrochemical experiments, chromatographic grade reagents were employed and further purification was performed when necessary. The elemental CHN analyses were performed on a Perkin-Elmer Elemental Analyser model 2400.

Synthesis

The precursor for the synthesis of *trans*–$[RuCl_2(pmp)_4]$, ruthenium blue, was prepared employing a method described in the literature,[12] with minor modifications. A blue ruthenium solution prepared from 260 mg (1, 0 mmol) of $RuCl_3{\cdot}3H_2O$, to which an ethanolic solution of 1300 mg (8, 0 mmoles) of pmp and hydroquinone (100 mg) was added, and kept under reflux for 40 min under argon protected from light (reflux times longer than 40 minutes might lead to the oxidation or polymerization of the pmp ligand). The reaction progress was monitored using thin layer chromatography (TLC), with dichloromethane or acetone as eluent. A clear separation between the product ($R_f \approx 1.0$) and the impurities (green compound) was observed. The reaction was also monitored by visible electronic spectroscopy, *via* the appearance of an intense band at 404 nm. The final solution was kept overnight in an ice bath, then filtered under vacuum. The solid was washed with ultra pure water (Millipore milli-Q) to remove traces of hydroquinone, followed by a large amount of ethanol/acetonitrile 1:1, until the green color of the filtrate disappeared.

The product was then dried with five washings with 20 mL of ethyl ether and recrystallized in toluene/dichloromethane, yielding good crystals. A yield of 52.5% was estimated, based on the amount of $RuCl_3{\cdot}3H_2O$ from the average of five syntheses. Results from CHN elemental analysis were in good agreement with the expected theoretical composition: *Anal.* Calcd. for $C_{40}H_{40}N_8Cl_8Ru$ (%): C, 59.70; H, 5.01; N, 13.92. Found: C, 59.93; H, 5.00; N, 13.87. Results from relative peak integration in ^1H NMR spectra reveal the presence of 40 protons. Results from ^1H NMR ($CDCl_3$) δ ppm *vs.* TMS: 4.90 $-CH_2$ (d, 8 H); 6.10 (s, 8 H); 6.60 (s, 8 H); 7.10 (d, 4 H); 7.30 (d, 4 H); 8.50 (m, 8 H). Qualitative analysis was performed by Scanning Electron Microscopy (SEM) and an EDAX microprobe attached to the SEM. The EDAX analysis of crystals showed the presence of Ru and Cl. The presence of C and N was also detected.

Spectroscopical Measurements

The vibrational spectral measurements were made on a Perkin-Elmer FT-IR spectrophotometer model 1GPC FT-IR in KBr pellets. The electronic spectra were obtained using a Hewlett Packard spectrophotometer, model HP8452A or SLM Aminco model DW-2000 TM, in quartz cuvets (path = 1 cm). The ^1H and ^{13}C NMR were obtained using a 300 MHz Brucker model AC200F in CD_3Cl.

Spectroelectrochemical Measurements

The Optically Transparent Thin Layer Electrode (OTTLE) experiments were performed on a Hewlett Packard spectrophotometer, model HP8452A, for optical monitoring, and a Pine Instrument Company bipotentiostat model RDE4 for electrochemical control. The assembly of OTTLE has been described in the literature.[13]

Electrochemical Measurements

Cyclic Voltammetry (CV), Pulse Differential Voltammetry (PDV), and Chrono-Amperometry (CA) were carried out at 25 °C with a Princeton Applied Research (PARC) Model 273A Potentiostat/Galvanostat, interfaced with a DOS compatible computer through a National Instrument General Purpose Interface Board (GPIB). Control of the instruments, data acquisition and processing were done using an EG&G model 270 (Research Electrochemistry Software). The cell and instrumentation setup have recently been completely described in the literature.[14] As support electrolyte, 0.1 mol dm^{-3} HTBA in dichloromethane was employed. All electrochemical experiments demanding an inert atmosphere were performed in a conventional three-electrode cell filled with argon (ultra-pure grade). CV measurements were made in several solvents and Pd, Pt, Au, ITO and a glassy carbon electrodes were used as the working electrode. Electropolymerization was performed by CV in a binary system formed by acetonitrile/dichloromethane.

RESULTS AND DISCUSSION

Synthesis of trans-[RuCl$_2$(pmp)$_4$]

The use of ruthenium blue as a precursor for the synthesis with the synthetic pathway used, yield as the main products the complex *trans*-[RuCl$_2$ (pmp)$_4$], as shown by ^{1}H and ^{13}C NMR, vibrational and electronic spectroscopy and cyclic voltammetry experiments. The use of hydroquinone to prevent intra- and inter-molecular polymerization through the pyrrolic moiety is fundamental in this synthesis. It is well known[8] that in acidic media pyrrol is susceptible to electrophilic attack at the α position of the pyrrolic ring. Such conditions exist when pmp is added to the ruthenium blue solution (pH ~ 2.0). A reaction without hydroquinone gives a very low yield with the production of a very large amount of an insoluble green compound of unknown composition. This byproduct is probably formed by polymerization cross-linking between the pyrrolic rings. In the same way, Wilkinson *et al.*[4] reported the formation of a highly insoluble, polymeric species for the synthesis of RuCl$_2$(2-vinylpyridine)$_2$. The product obtained from the synthesis without hydroquine shows a visible electronic maximum at 666 nm, and is insoluble in a broad range of solvents. Another green byproduct (660 nm) was observed during filtration (filtration residue) and also in the recrystallization solutions. This green byproduct was also found in syntheses involving other ligands.[20] The complex acquires a yellow color when dissolved in a binary solution of toluene and dichloromethane, and changes to a greenish color over time (λ_{max} = 660 nm). Upon addition of a reducing agent, such as zinc amalgam in acidic medium, a new band appears at 404 nm attributed to *trans*-[RuCl$_2$ (pmp)$_4$]. Taube[15] reported that the *cis*-[RuCl$_2$(py)$_4$] complex in methylene chloride turns green upon being exposed to air.

Infrared Spectroscopy

The IR spectrum of this complex differs slightly from the free ligand[21] (non-coordinated ligand), indicating that most of the vibrational modes are preserved, with small shifts toward either longer or shorter wavelengths indicating coordination of the ligand pmp, to the metallic center. The main characteristics bands are located at 723 cm^{-1} (assigned to the asymmetric angular deformation in the plane of the CH_2 group) and at 910 cm^{-1} (assigned to the symmetrical C–H angular deformation outside the plane). The most prominent observed changes are bands at 632 cm^{-1} and 450 cm^{-1}, assigned to the coordinated pyridinic ring. The same bands in the non-coordinated ligand are located at 605 cm^{-1} and 405 cm^{-1}. The same shifts were reported by Clark[16] for *trans*-$[RuCl_2(py)_4]$ and are very sensitive to the complex symmetry. Such shifts are also found in other octahedral complexes.

^{13}C NMR of trans–$[RuCl_2(pmp)_4]$

Taube and Raichart[15] showed that the geometry (*cis* or *trans*) of complexes $[RuX_2(L)_4]$ can be determined from ^1H NMR spectroscopy: the neighboring protons to the pyridinic nitrogen ring are sensitive to the metallic center and the halogen. Complexes of *cis* geometry present two ^1H NMR peaks of 1:1 relative intensity for the protons in the vicinty of N, whereas for *trans* geometry, only one resonance is observed. The same is expected for ^{13}C NMR, as shown in Figure 2. The integrity of the pyrrole moiety is confirmed from a peak at δ 121.33 (C7 and C10) as well as δ 109.71 (C8 and C9). The carbon peaks C1 and C5 are shifted to the weak field as compared to the non-coordinated ligand. Atoms located far from the ruthenium center are not affected. Measurements taken in our laboratory for *trans*-$[RuCl_4(py)_4]$ also show a shift (around 8 ppm for C1 and C5) due to coordination. The sharp pattern of the ^1H NMR peaks are characteristic of a diamagnetic species, d^6 low spin, which was confirmed by EPR spectroscopy.

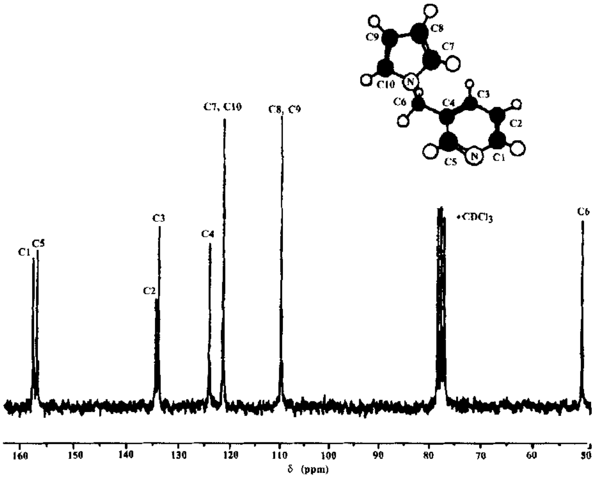

FIGURE 2 ^{13}C NMR spectra in $CDCl_3$.

The relative integration of ^{1}H NMR peaks show the presence of 40 protons. The presence of pyrrolic protons clearly indicates the integrity of the pyrrolic ring and rules out *inter–* or *intra–* polymerization by attack on the α or α' positions of the pyrrole ring. ^{1}H NMR spectroscopy obtained from samples prior to recrystallization shows a broadening of the peaks in the low field region, indicating the presence of paramagnetic impurities, probably Ru(III) species.

Electronic Spectroscopy

The electronic spectrum of *trans*-$[RuCl_2(pmp)_4]$ in CH_2Cl_2 shows two visible transitions, a strong band at 404 and a weak band at 475 nm, which are slightly shifted to the red region (about 6 nm) compared with the value obtained in our laboratory (398 nm) for *trans*-$[RuCl_2(py)_4]$. Poddar and Agarwala[17] reported the presence of two low intensity transitions between 600 and 700 nm, for *trans*-$[RuCl_2(py)_4]$; these absorptions were not found in this work.

Electrochemistry

Figure 3 shows a typical cyclic voltammogram in dichloromethane, obtained at a scan rate of 500 mV s^{-1} and showing an anodic potential of $\varepsilon_a = 0.59$ V. This potential corresponds to the *trans*–$[RuCl_2(pmp)_4]^{0/+}$ couple, while the wave at cathodic potential $\varepsilon_c = 0.47$ V corresponds to a *quasi*-reversible process of *trans*-$[RuCl_2(pmp)_4]^{0/+}$. Several scans performed at negative potentials show no presence of voltammetric waves. The same behavior was observed by Mukaida[12] for *trans*-$[RuCl_2(py)_4]$, as well as for the new complexes of this family with carboxylate piridinic ligands synthesized in our laboratory.[20] Analysis of the cyclic voltammetric response, with scan rates varying from 25 to 500 mV s^{-1} showed that (i) the τ_{pc}/τ_{pa} current ratio is equal to 1, (ii) the current function $\tau_{pa}/v^{1/2}$ remains substantially constant, (see insert in Figure 3) and (iii) the peak-to-peak separation, ΔE_p, progressively increases from 92 mV to 150 mV, suggesting reorganization energy accompanying the electron transfer due to significant structural reorganization. The uncompensated solution resistance was corrected by using the algorithm CONDECON[22] to an extent that all increases in the ΔE_p at high scan rate could not be attributed to the solution resistance. The integration of the area under the anodic (Q_a) and cathodic (Q_c) peaks shows a charge ratio $(Q_a)/(Q_c)$ close to unity at scan rates ranging from 25 to 500 mV s^{-1}. A value of $E^{1/2} = 0.53$ V *vs.* NHE was obtained from both techniques and the Differential Pulse Voltammetry (DPV) and CV are 170 mV higher than that found[12] for *trans*-$[RuCl_2(py)_4]$. The experimental voltammograms correlate very well with that analyzed according to the powerful algorithm COOL[23] (Figure 3) for a *quasi*-reversible electrochemical mechanism.

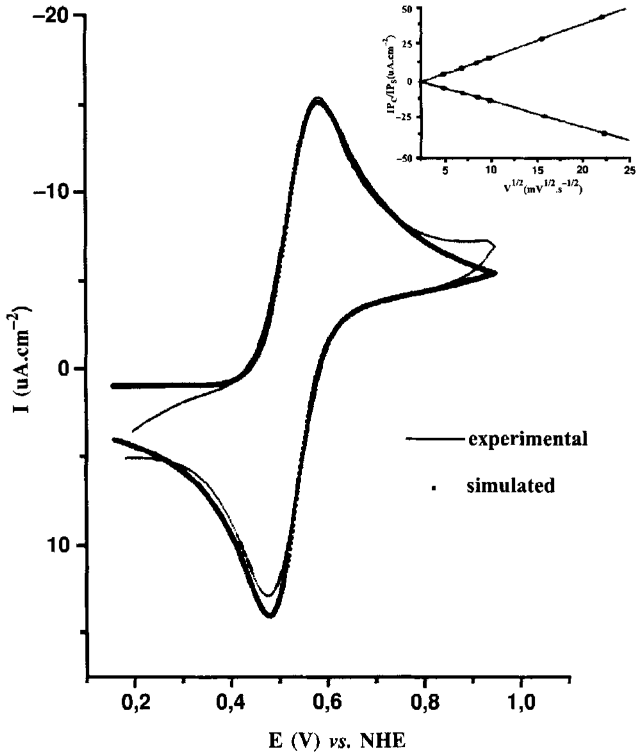

FIGURE 3 Cyclic Voltammetry obtained for redox processes of *trans*-$[RuCl_2(pmp)_4]^{0+}$ in dichloromethane solution 0.1 mol dm^{-3} HTBA (solid line) and simulated by COOL algorithm (dashed line).

$$\kappa = k_{s,h}^{0} / (D_{ox}^{1-\alpha} \times D_{red}^{\alpha}) \qquad (1)$$

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C^0 v^{1/2} \qquad (2)$$

Data in Table I display the theoretical parameters used to fit the experimental curve in Figure 3. The heterogeneous rate constant for the electron transfer, 2.31×10^{-4} cm s^{-1}, was estimated from the fitting parameters, $\log(k \cdot \sqrt{tp})$which are related to the electron transfer heterogeneous constant, k_{sh}^0, through κ: where the coefficient constant D is related to the reduced and oxidized electroactive species, α is the charge transfer coefficient and is associated to a *quasi*-reversible redox process, and tp is the step time related to the cyclic voltammetric experiment. The values of $D_{ox} = D_{red} = 1.73 \times 10^{-8}$ cm^2 s^{-1} were found from the slope in

TABLE I Theoretical fitting parameters for a *quasi*-reversible process for the experimental cyclic voltammetry of *trans*-$[RuCl_2(pmp)_4]^{0/+}$

Scan rate, v, mV.s^{-1}	*log(k · √tp)*	κ	*(1 - corr coef) × 10*^{3}	α	$t_p \times 10^3$ *s*	$k_{s,h}^0 \times 10^4$ *cm.s*$^{-1}$
50	– 0.523	1.495	8.22	0.365	40	1.97
250	– 0.752	1.980	7.98	0.346	8	2.60
500	– 0.947	1.788	8.90	0.378	4	2.35

the insert of Figure 3 and the Randles-Sevick equation 2,[24] where i_p is the peak current (A), n is the number of transferred electrons, A is the electrode area (cm^2), D is the diffusion coefficient of the reduced and oxidized species ($cm^2\ s^{-1}$), C^0 is the bulk concentration of the same species (mol dm^{-3}), and v is the scan rate (V s^{-1}).

Spectroelectrochemistry

The spectroelectrochemistry was conducted according to the procedure described in the literature[13] and was performed in the potential ranging from 0.15 to 0.80V *vs.* NHE. There is a gradual disappearance of the bands located at 404 and 475 nm as the oxidation proceeds (Figure 4). The appearance of a new band at 302 nm is due to the formation of Ru(III). The isoelectronic point at 340 nm indicates the absence of any intermediate during the redox proess. At applied potentials lower than $E^{1/2}$, the spectra due to the reduced species are readily obtained. The system follows the Nernst Equation with a value of $E^{1/2}$ = 0.58 V *vs.* NHE from a plot of $E_{applied}$ *vs.* Log[0]/[R] and $E^{1/2}$ in close agreement with the value obtained from CV and PDV. The plot is linear with slope of 59 mV corresponding to n = 1 electron.

FILM-FORMING ELECTROPOLYMERIZATION

The electropolymerization of *trans*–$[Ru(pmp)_4Cl_2]$ was performed in acetonitrile/dichloromethane (1:1) solvent by repeated cyclic scanning of potential (– 0.46V to 1.35V) on a platinum electrode. Typical results are shown in Figure 5 in which repeated scanning results in a continuous increase in the size of the CV peaks, indicating the formation of an electroactive film at the surface of the platinum electrode. The main electrochemical process corresponds to the Ru^{III}/Ru^{II} couple at E_{pc} = 368mV and E_{pa} = 465mV. A second wave is seen at E_{pc} = 299 mV and E_{pa} = 500mV, which is presumed to be due to a polymer chain redox couple. The increase in size of the cyclic voltammetry peaks clearly demonstrates the

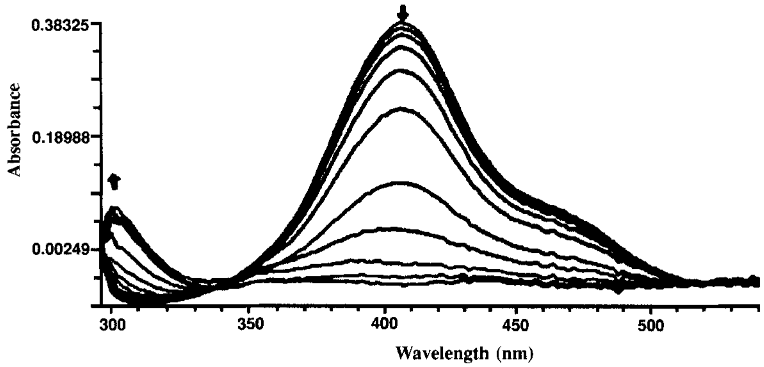

FIGURE 4 Spectroelectrochemistry obtained for the redox process *trans*–$[Ru^{II}Cl_2(pmp)_4]^{0/+}$.

formation and growth of a polymer film on the electrode surface. Note that the form of the anodic peak. current of the redox couple Ru(III)/Ru(II) is different to that found for the cathodic peak current. Systems presenting cathodic and anodic peaks with difference in their symmetry occur basically when one of the redox states on the polymeric backbone is neutral, as may be the case of the poly–*trans*–$[RuCl_2(pmp)_4]^{0/+}$ redox couple. After a period of scanning, the electrode, which is covered by a golden–yellow thin polymeric film, is transferred with thorough rinsing to a clean MeCN/ 0.1 mol dm^{-3} HTBA solution (Figure 6). It is surprising that the potential values of the different redox systems are very close to those observed for the corresponding monomeric complexes in solution (Figure 4).

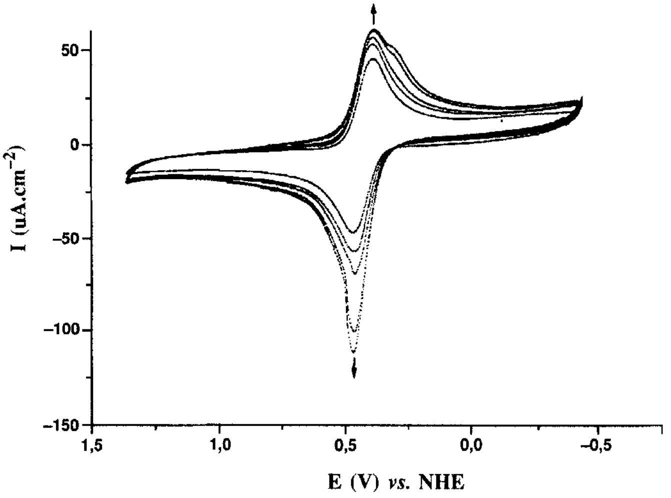

FIGURE 5 Cyclic voltammogram depicting the growth of the *trans*–$[RuCl_2(pmp)_4]^{0/+}$ peak during film formation from 10^{-3}mol.dm^{-3} in MeCN/CH_2Cl_2 (2:1) / 0.1 mol dm^{-3} HTBA; scan rate 50 mV s^{-1}, electrode area = 0.11 cm^2.

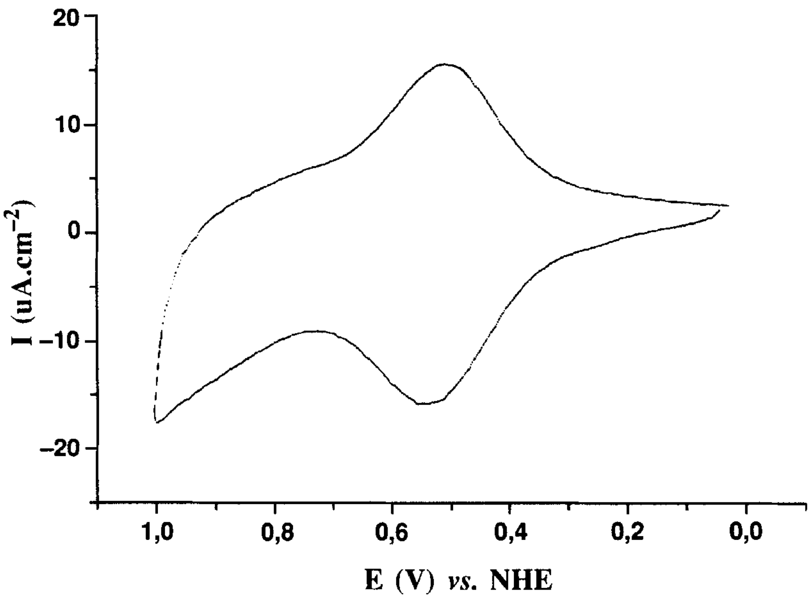

FIGURE 6 Cyclic voltammogram of a poly-*trans*-[$RuCl_2(pmp)_4]^{0/+}$ modified electrode in MeCN/ 0.1 mol dm^{-3} HTBA; scan rate 50 mV s^{-3}.

The Ru(III)/Ru(II) peak separation is 46 mV and indicates that a monolayer is not formed (ΔE_p = 0 mV) as indicated in Figure 6. Many scans can be repeated without any change of the cyclic voltammetric curve. The yellow film adheres strongly to the electrode surface. The estimated surface coverage is ~ 7.3 x 10^{-9} mol cm^{-2}.

Results from electropolymerization of *trans*-[$RuCl_2(pmp)_4$] obtained at positive potentials will be the subject of a further report.

CONCLUSIONS

The preparation of *trans*-[$RuCl_2$ $(pmp)_4$] from a ruthenium blue precursor shows good yield and stereoselectivity, as well as good ligand integrity upon addition of a small amount of hydroquinone. Data from electronic spectroscopy, spectroelectrochemistry and cyclic voltammetry, show typical behavior for *trans*-[$RuCl_2(pmp)_4]^{0/+}$ with a reversible redox process centered at the metal. We have demonstrated the successful preparation of a modified electrode by electro-polymerization of *trans*-[$RuCl_2(pmp)_2]^{0/+}$. Further work is planned to improve the characterization of the formed film and to incorporate it into copolymers of an electronically conductive polypyrrole backbone.

Acknowledgments

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