

Synthesis, characterization, electropolymerization, and possible utilities of a new ruthenium–thiophene complex

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ABSTRACT: $[\text{RuCl}_2(p\text{-cymene})]_2$ was reacted with silver triflate and thiophene to give the sandwich complex $[\text{Ru}(\eta^5\text{-C}_4\text{H}_4\text{S})(\eta^6\text{-}p\text{-cymene})](\text{PF}_6)_2$, which was characterized with NMR spectroscopy ($^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and $^{31}\text{P-NMR}$), Fourier transform infrared spectroscopy, elemental analysis, and cyclic voltammetry. The behavior of this new complex in dimethyl sulfoxide with regard to the amount of absorbed water was investigated by both NMR and cyclic voltammetry; the formation of other species that affected electropolymerization was demonstrated. However, under optimal working conditions (in an anhydrous medium), the complex was successfully immobilized on a platinum electrode via an electro-oxidation pathway through the thiophene ligand. This generated a highly stable, electroactive polymer film. Its response to the doping–undoping (charge–discharge) and redox processes, added to its high stability, promises important applications for this novel material. Moreover, this opens up the possibility of testing other compounds, such as $[\text{Ru}(\eta^5\text{-thiophene})(\eta^6\text{-arene})]$, that were previously synthesized and reported for their electropolymerization and use as sensors according to their redox properties. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43559.

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INTRODUCTION

Nowadays, many research works are focused on the preparation, characterization, and application of conductive polymers, for example, polythiophenes, polyanilines, and polypyrroles.^{1–7} In general, conductive polymers possess the same electronic structure, which is purely organic;^{8–14} this is the reason for their electrical conductivity, low ionization potential, and high electron affinity. An important advance in the development of these conductive polymers or polyheterocycles took place in 1979, when highly conductive and homogeneous films of pyrrole polymers were produced through electrochemical oxidation.¹⁵ This served to indicate, at that time, the interest in electrochemically generated polyaniline;¹⁶ the study was thus applied to many other aromatic systems, for example, thiophene and derivatives, through the investigation of their properties.¹⁷ Many of these polymerizable heterocycles could be coordinated to transition metals to produce conducting metallopolymers with new electronic and optical features.^{18–23}

By the 1980s, metal–thiophene interaction had aroused great interest,^{24,25} and thiophenes showed four bonding modes to

metals,^{26,27} η^5 being the most common coordination mode. In this respect, the studies of Rauchfuss and coworkers^{27–32} on $[\text{Ru}(\eta^5\text{-thiophene})(\eta^6\text{-arene})]$ structures were important. These compounds proved to be susceptible to base-catalyzed hydrolysis and aminolysis, and this led to C–S bond breakage. In addition, they have been relevant in desulfurization catalysis.^{33,34} Furthermore, such complexes have been demonstrated to be of interest in asymmetric synthesis^{35,36} and for their nonlinear optical properties.³⁷

In this article, the synthesis and characterization of a novel ruthenium–thiophene complex, whose electrochemical properties in dimethyl sulfoxide (DMSO) were studied by cyclic voltammetry, are described. The surface modification of a platinum (Pt) electrode with the same compound was also studied with electropolymerization. The formation of a new conducting polymer was revealed, and the electrode modified with this product was characterized with their possible applications taken into account,^{38,39} although in this case, it did not seem to be the optimal deposit. Nevertheless, this opens up the possibility of testing other compounds, such as $[\text{Ru}(\eta^5\text{-thiophene})(\eta^6\text{-$

arene)], which were previously synthesized and reported to be electropolymerized and tried as sensors according to their redox properties.

EXPERIMENTAL

Preparation and Tools

The analytical-grade reagents were used as received. The reactions were conducted under a pure nitrogen atmosphere in freshly distilled and oxygen-free solvents with the standard Schlenk technique. The $[\text{RuCl}_2(p\text{-cymene})]_2$ complex was prepared according to the reported method,⁴⁰ and the solvents were freshly distilled before use.⁴¹

For electrochemical experiments, DMSO (Aldrich, 99.7%), which was stored over molecular sieves, and tetrabutyl ammonium hexafluorophosphate (TBAPF₆; Aldrich, 98%), which was dried previously at 120 °C, were used as the solvent and supporting electrolyte, respectively.

¹H-NMR and ¹³C-NMR spectra were recorded at room temperature on a Bruker Advance 200 spectrometer operating at 200 MHz and 25 °C. The sample peak positions were relative to tetramethylsilane and were calibrated against the residual solvent resonance (¹H-NMR) or the deuterated solvent multiplet (¹³C-NMR). The coupling constants (*J*) are reported in hertz. The abbreviations used to denote the multiplicity of a particular signal were s (singlet), d (doublet), and m (multiplet). IR spectra were recorded in KBr disks on a Bruker Vector 22 Fourier transform infrared spectrometer over the 4000–250-cm⁻¹ range. Elemental analyses (C, N, H, and S) were performed on a CE Instruments EA 1108 elemental analyzer. Cyclic voltammetric measurements were conducted with a Voltalab PG2100 potentiostat at room temperature (20 °C) under a high-purity argon atmosphere. A conventional three-electrode system was used with an anchor-type three-compartment electrochemical cells. A Pt disk (geometric area = 0.07 cm²) was used as a working electrode, a Pt wire coil with a large geometric area was used as a counter electrode, and Ag/AgCl in a tetramethyl ammonium chloride solution to match the potential of a saturated calomel electrode (SCE) was used as a reference electrode. A 0.01 mol/L TBAPF₆ solution was used as the supporting electrolyte.

Polymer films were deposited by a potentiodynamic (cyclic voltammetry) method under the previously optimized experimental conditions, namely, with a potential window of 1.35 to -0.8 V and a scan rate of 0.05 V/s (50 consecutive cycles). The working solution consisted of 1×10^{-3} mol/L $[\text{Ru}(\eta^5\text{-C}_4\text{H}_4\text{S})(\eta^6\text{-}p\text{-cymene})]^{2+}$ plus 0.01 mol/L TBAPF₆ in anhydrous DMSO. Subsequently, the $[\text{Pt}/p\text{-Ru}(\eta^5\text{-C}_4\text{H}_4\text{S})(\eta^6\text{-}p\text{-cymene})]^{2+}$ -modified electrode response was studied with a 0.01 mol/L TBAPF₆ solution in DMSO, and images from the electrode surface were obtained on a Leo VP1400 scanning electron microscope.

Synthesis of $[\text{Ru}(\eta^5\text{-C}_4\text{H}_4\text{S})(\eta^6\text{-}p\text{-cymene})](\text{PF}_6)_2$ (**1**)

The compound was prepared by the reaction of $[\text{RuCl}_2(p\text{-cymene})]_2$ (0.115 g, 0.190 mmol) with AgOSO₂CF₃ (0.191 g, 0.740 mmol) in dichloromethane (CH₂Cl₂; 18 mL) in the dark for 2 h. The orange suspension was filtered to remove the precipitated AgCl. The orange filtrate was stirred with an excess of

thiophene (1 mL) for 16 h. The solvent and residual thiophene removal was accomplished with a syringe, and the remaining brown oil was extracted with ethanol. The ethanolic solution was filtered through celite, and the filtrate was treated with an excess of NH₄PF₆ solution. After overnight storage at -20 °C, a light yellow solid was collected by filtration; the product was then washed with CH₂Cl₂ (2 × 2 mL) and diethyl ether (2 × 3 mL) and finally vacuum-dried.

Yield = 77.8%. ANAL. Calc. for C₁₄H₁₈F₁₂P₂RuS (molar mass (*M_r*) = 609.36 g/mol): C, 27.6%; H, 2.95%; S, 5.25%. Found: C, 28.1%; H, 2.82%; solubility (S), 5.30%. *S*_{20 °C, DMSO} = 33.3 mg/mL. *S*_{20 °C, CH₃CN} = 30 mg/mL. Fourier transform infrared (KBr, cm⁻¹): 3116.5 [*ν*(=C-H)], 839.5 [*ν*(P-F)PF₆], 557.6 [*ν*(=C-H)]. ¹H-NMR (200 MHz, acetone-*d*₆, *δ*, ppm): 7.48 (m, *J* = 4.0 Hz, 4H, C₄H₄S), 7.09 (m, 4H, *p*-cymene), 3.14 [m, *J* = 6.0 Hz, 1H, CH(CH₃)₂], 2.65 (s, 3H, CH₃), 1.43 [d, *J* = 8.0 Hz, 6H, CH(CH₃)₂]. ¹³C-NMR (200 MHz, acetone-*d*₆, *δ*, ppm): 20.03 (s, CH₃Ph of *p*-cymene); 23.01 [s, (CH₃)₂CHPh of *p*-cymene]; 32.89 (s, -CH- of *p*-cymene); 92.67, 97.54 (s, aromatic carbons of *p*-cymene); 94.66, 94.78 (aromatic carbons of thiophene); 122.69, 122.81 (quaternary carbons of *p*-cymene). ¹⁹F(¹H)-NMR (200 MHz, acetone-*d*₆, *δ*, ppm): 103.59, 107.35 (s, PF₆).

NMR Study of Stability of **1** in DMSO and Air

Compound **1** (6.3 mg, 0.010 mmol) was dissolved in 0.5 mL of hexadeuterated dimethyl sulfoxide (DMSO-*d*₆) in a 5-mm NMR tube. Significant changes were observed from the start of the study until more than 24 h had passed.

RESULTS AND DISCUSSION

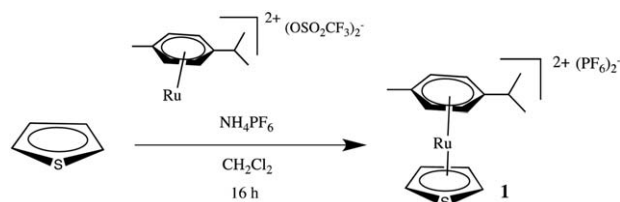
Synthesis and Structural Characterization

On the basis of previous results regarding the obtaining of ruthenium complexes with coordinated thiophenes,^{27–32,37} the synthesis of the new complex **1** was tested by the reaction of $[\text{RuCl}_2(p\text{-cymene})]_2$ in CH₂Cl₂ with AgOSO₂CF₃ to generate *in situ* $[\text{Ru}(p\text{-cymene})(\text{OSO}_2\text{CF}_3)_2]$; this was followed by the addition of thiophene (Scheme 1). Because certain triflate salts are usually hygroscopic, one often needs to exchange the counterion of the hexafluorophosphate triflate. Thus, in this study, a lemon yellow, air-stable solid (yield = 77.8%), which was isolated as a hexafluorophosphate salt, was obtained. Its structure was characterized by NMR, elemental analysis, and cyclic voltammetry.

Both the ¹H-NMR and ¹³C-NMR spectra showed signals within the characteristic region of both ligands in similar complexes.^{29,36} In addition, the ¹⁹F-NMR spectrum, which showed two singlets (103.59 and 107.35 ppm), and the IR spectrum, with a P-F characteristic band at 839.5 nm, confirmed the presence of ionic species of PF₆⁻ as counterions in the structure proposed for the same.

Electrochemical Characterization and Electropolymerization of Complex **1**

The electrochemical behavior of complex **1** was studied by cyclic voltammetry in an anhydrous DMSO solution containing 1×10^{-3} mol/L $[\text{Ru}(p\text{-cymene})(\eta^5\text{-C}_4\text{H}_4\text{S})]^{2+}$ and 1×10^{-2} mol/L TBAPF₆. The responses were determined on a Pt electrode at a 100 mV/s scan rate between -1.0 and 0.2 V versus SCE, with the first sweep



Scheme 1. Synthesis of complex **1**.

being anodic. Figure 1 shows the cyclic voltammogram of complex **1**, wherein an electrochemically irreversible redox couple (peak potential difference (ΔE_p) = 0.401 V), ascribed to the Ru(II)/Ru(III) couple [Figure 1(A)], was observed. When we compared the complex reduction potential (reduction potential (E_{red}) = -0.592 V) with the reduction potential of the $[\text{Ru}(\text{NH}_3)_6]$ complex [E_{red} = -0.412 V; Figure 1(B)], we found that in complex **1**, the metal reduction occurred at more negative values (E_{red} shift = 180 mV).

In Figure 2, cyclic voltammograms of the same solution run on Pt at different ν values (20–180 mV/s) are shown. An anodic peak shift toward more positive potentials as ν increased was observed. Furthermore, both the oxidation and reduction peak currents varied linearly with scan rate square root; this means that the redox process took place under diffusion control. This behavior suggested a mobility of the supporting electrolyte counterions necessary for the charge transport or the retention of the electroneutrality of the electrode surface during the redox process.^{42–44}

On the other hand, the $[\text{Ru}(p\text{-cymene})(\eta^5\text{-C}_4\text{H}_4\text{S})]^{n+}$ polymer was obtained by electrooxidation with successive voltammetric scans between -0.8 and 1.35 V at a 50 mV/s scan rate, the first sweep in the anodic direction. The working solution and conditions were those used in the previously described cyclic voltammetry study. The voltammograms recorded during the polymer electrosynthesis are shown in Figure 3. Three well-defined peaks were observed. The first peak current, corresponding to the electrooxidation process of thiophene in the complex, increased after each successive cycle, whereas the second peak, occurring at a less positive potential, was ascribed to the doping–undoping process of the formed polymer film (appearing from the second cycle). These profiles entailed a deposit growth on the Pt electrode surface. A third peak at a more negative potential,

corresponding to the Ru(II)–Ru(III) couple, was also observed; this was consistent with the proposed structure, wherein thiophene was bound to the metal through its π cloud by η^5 bonding.^{26,27}

In addition, the scanning electron microscopy image of the Pt-modified electrode is depicted in Figure 4. This image allowed us to corroborate the formation of a homogeneous deposit on the Pt surface, which was fully coated with granules of different sizes; this was ascribed to the deposit being generated through progressive nucleation.

Figure 5(A) shows the voltammetric response of the previous deposit, that is, the $p\text{-}[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\eta^5\text{-C}_4\text{H}_4\text{S})]^{n+}$ polymer modified electrode in a solution containing just the supporting electrolyte, where both the metal redox couple and polythiophene characteristic doping–undoping were observed.^{45–47} The redox couple described for the Ru(II)/Ru(III) pair was observed at negative potentials [Figure 5(B)], with the difference between oxidation potential peak ($E_{p(\text{ox})}$) (-0.50 V) and reduction potential peak ($E_{p(\text{red})}$) (-0.95 V) being 0.45 V; this indicated that the process remained electrochemically irreversible, but the reduction potential shift toward more negative values was much higher. This showed that when it was polymerized, the complex became even more stable.

On the other hand, in the enlarged Figure 5(C), the thiophene doping–undoping process was observed. The doping–undoping charges ratio close to 1 revealed a chemically reversible process; this allowed us to envision its use in rechargeable batteries.

However, it is worth noting that when the charges of both processes were compared, the metal redox couple was much more important than that of the thiophene doping–undoping process; this suggested that these $p\text{-}[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\eta^5\text{-C}_4\text{H}_4\text{S})]^{n+}$ films are potential candidates for obtaining redox polymers. Nevertheless, also interesting was a previous study concerning the stability of the doping–undoping process with regard to the number of cycles, with a view to implement its use in battery cathodes, as usually done with polythiophenes.³⁹

Figure 6(A) shows the cyclic voltammograms corresponding to the p -doping–undoping process during 1000 charge–discharge successive cycles; this corroborated the high stability of the film. Likewise, Figure 6(B) shows that the chemical reversibility of

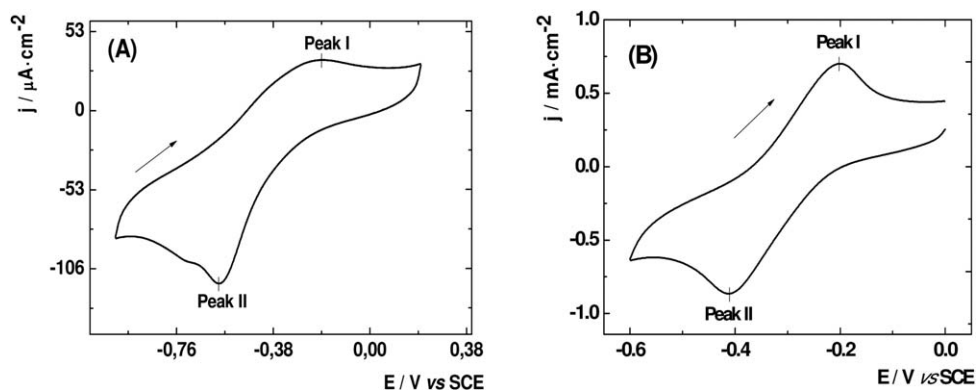


Figure 1. Cyclic voltammograms of (A) 1.0×10^{-3} mol/L $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\eta^5\text{-C}_4\text{H}_4\text{S})]^{2+}$ complex in 1×10^{-2} mol/L TBAPF₆ on a Pt electrode and (B) 1.0×10^{-3} mol/L $[\text{Ru}(\text{NH}_3)_6]$ complex in 1×10^{-2} mol/L TBAPF₆ on a Pt electrode ($\nu = 100$ mV/s). j , current density; E , potential.

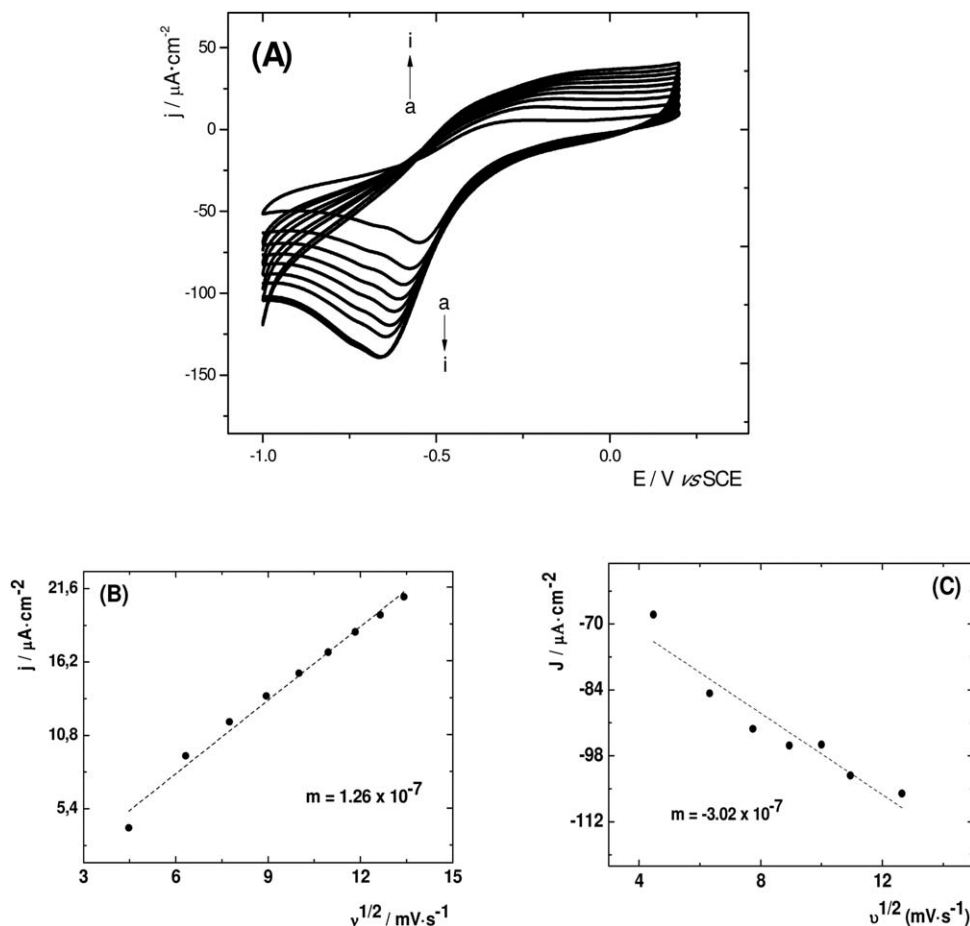


Figure 2. (A) Cyclic voltammograms of 1×10^{-3} mol/L $[\text{Ru}(\text{h}^6\text{-}p\text{-cymene})(\text{h}^5\text{-C}_4\text{H}_4\text{S})](\text{PF}_6)_2$ complex in DMSO on Pt at potential scan velocity (ν) values of (a) 20, (b) 40, (c) 60, (d) 80, (e) 100, (f) 120, (g) 140, (h) 160, and (i) 180 mV/s. (B,C) Peak current versus the square root of the scan rate: (B) oxidation potential (E_{ox}) > and (C) reduction potential (E_{red}).

this film was not affected during the study. It was verified, however, that the profile became stabilized after the first few cycles, probably because of film reordering, and consequently, before

use it in this application, the modified electrode needed to be stabilized. After stabilization, a constant percentage of charge was attained, even after the 1000th cycles.

With these results, it would be interesting to test this electrode as a cathode in batteries, but its high cost does not justify delving deeper into that application. It is important to know that

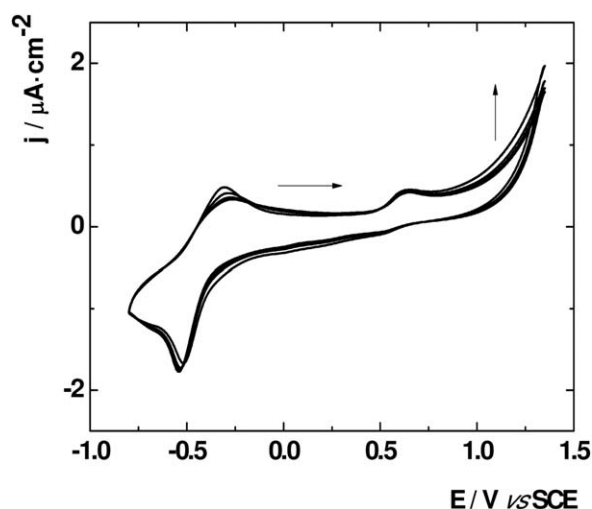


Figure 3. Voltammetric electrooxidation profile of $[\text{Ru}(\text{h}^6\text{-}p\text{-cymene})(\text{h}^5\text{-C}_4\text{H}_4\text{S})]^{n+}$ on Pt in a supporting electrolyte ($\nu = 50$ mV/s). j , current density; E , potential.

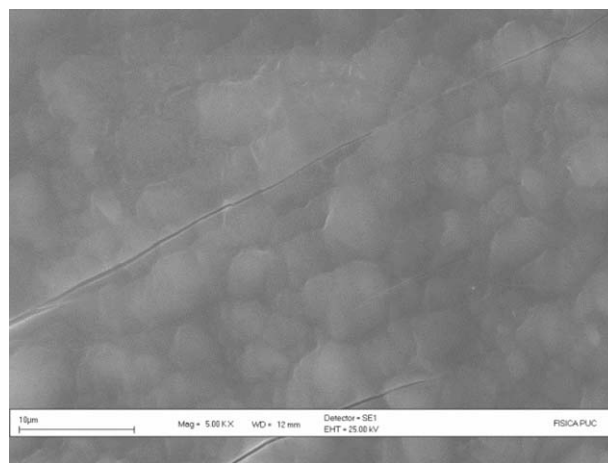


Figure 4. Scanning electron microscopy image of a Pt/polymer-modified electrode.

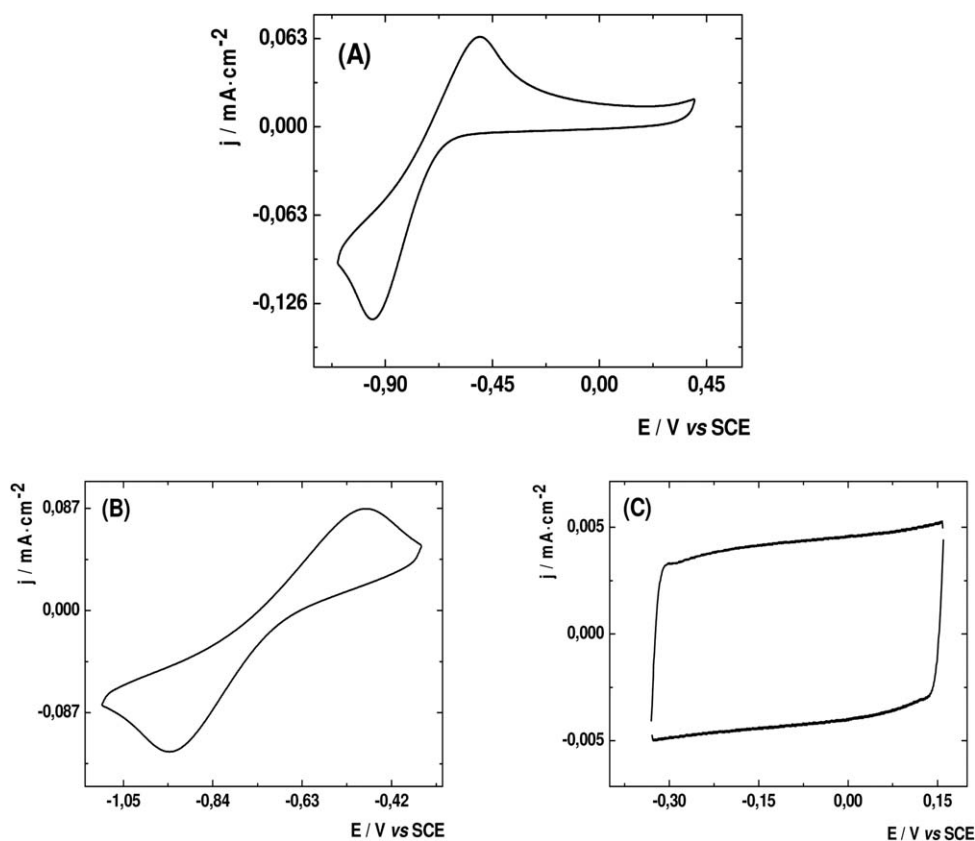


Figure 5. Voltammetric response of a p -[Ru(h^6 - p -cymene)(h^5 -C₄H₄S)]^{*n*+} modified electrode in a supporting electrolyte: (A) -1.10 to 0.40 V, (B) -1.10 to -0.35 , and (C) -0.33 to 0.16 V ($v = 100$ mV/s). j , current density; E, potential.

this behavior, which was observed only as part of the characterization, might have an interest that today we do not see. This result contributes even more when the redox couple is considered because it opens up the possibility of proposing such modified electrodes as sensors toward some desired analyte with an *a priori* certainty of its great stability.

Stability of the Complex in DMSO and Air

Figure 7 shows the ¹H-NMR spectra as a function of the time, where it is demonstrated that when the study was done in the

presence of air, the complex was unstable in DMSO. In similar complexes, a trend to undergo nucleophilic attack on both rings²⁶ was reported; this implied that in this study, it would behave similarly. When compared to other complexes where the attack usually occurred preferentially on the thiophene ring, in this case, surprisingly, no single attack on the thiophene ring took place. Instead, no p -cymene ligand signals were observed, whereas new signals appeared suggesting the formation of novel derivative complexes. Nevertheless, because of the complexity of these mixtures, it was impossible to satisfactorily separate and purify them.

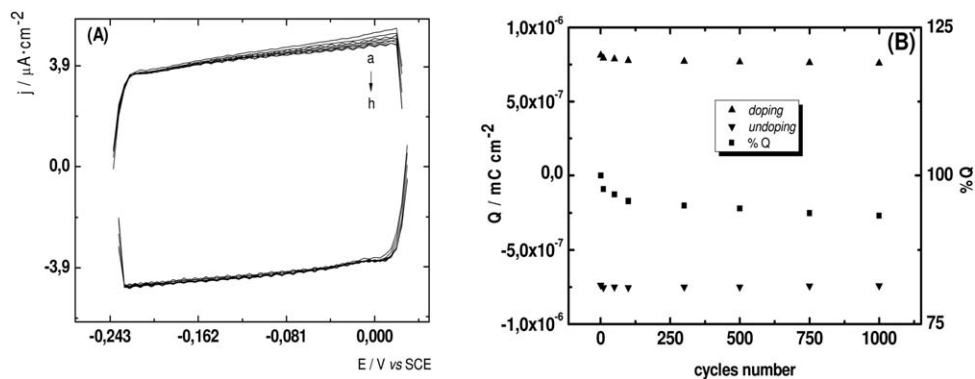


Figure 6. (A) Voltammetric response of the p -doping-undoping process of Pt/ p -[Ru(h^6 - p -cymene)(h^5 -C₄H₄S)]^{*n*+} in a supporting electrolyte ($v = 100$ mV/s) and (B) graphic representation of the p -doping-undoping charge and percentage of the charge versus the number of successive voltammetric cycles. j , current density; E, potential.

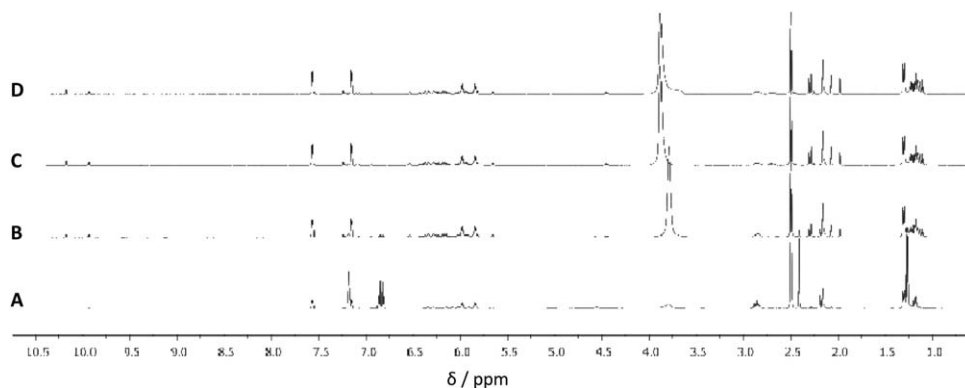


Figure 7. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$) study of the complex air stability of **1** as a function of time: (A) 2, (B) 4, (C) 6, and (D) 24 h.

Instability in this medium and in air was also found when the complex electropolymerization was carried out; it was possible to verify how the electropolymerization profiles changed as the humidity of the medium increased. Thus, the emergence of new species had an influence on the electropolymerization process (Figure 8) when the chemical environment around the metal and, therefore, the product(s) were varied.

It is worth noting how, as the amount of water in the medium increased, for example, after 24 h, a remarkable increase in the current was obtained and how the oxidation and reduction potentials of the Ru(II)/Ru(III) redox couple shifted toward a less positive potential; this indicated a strong presence of water in the solution that hindered the electropolymerization process because of solvent discharge. In summary, to ensure electropolymerization reproducibility and obtaining the polymer described and studied herein, the absence of water in the electrolytic medium in which the polymerization occurred was an absolute requirement.

CONCLUSIONS

A novel ruthenium complex, **1**, containing an electropolymerizable thiophene ligand was synthesized and characterized. The complex was successfully polymerized with electrooxidation on a Pt electrode. The electropolymerization had to be conducted in anhydrous medium because moisture absorption by the sol-

vent, DMSO, interacted with the monomer to form other difficult to separate species. Once the resulting polymer film on the electrode was prepared, it was characterized by scanning electron microscopy and cyclic voltammetry; these demonstrated it to be electroactive and highly stable. Finally, we found great stability in the doping–undoping process of the $p\text{-[Ru}(\eta^5\text{-}p\text{-cymene})(\eta^5\text{-C}_4\text{H}_4\text{S})]^n+$ modified electrode with regard to the number of cycles; this is an interesting property in a view of its implementation in battery cathodes. In addition and most important, this finding opens up the possibility that other such compounds, for example, $[\text{Ru}(\eta^5\text{-thiophene})(\eta^6\text{-arene})]$, which was already reported, may be electropolymerized and tested for some possible applications of these materials.

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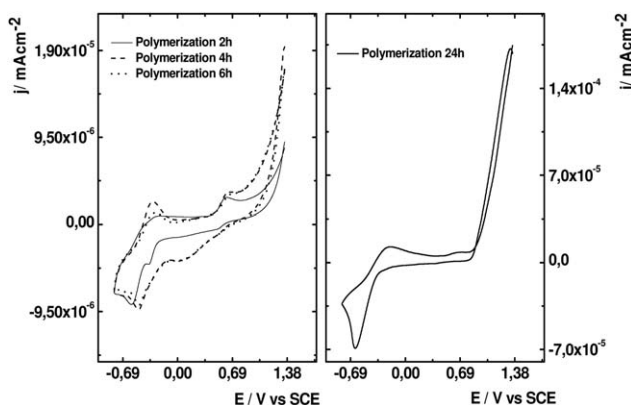


Figure 8. Variation of the voltammetric electrooxidation profile of $p\text{-[Ru}(\eta^6\text{-}p\text{-cymene})(\eta^5\text{-C}_4\text{H}_4\text{S})]^n+$ as a function of the humidity present in the electrolytic medium (atmospheric exposure time; $v = 50$ mV/s).

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