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SYNTHESIS, ELECTROCHEMICAL CHARACTERIZATION AND POTENTIOMETRIC TITRATION OF *trans*-[RuCl₂(L)₄] COMPLEXES (L = PYRIDINE DERIVED LIGANDS: 3-PYRIDINECARBOXYLIC ACID AND 4-PYRIDINECARBOXYLIC ACID)

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**SYNTHESIS, ELECTROCHEMICAL
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In this work we report the synthesis, spectroscopic characterization, potentiometric titration and electrochemical studies performed on *trans*-[RuCl₂(nic)₄] (I) and *trans*-[RuCl₂(*i*-nic)₄] (II) complexes, where nic = 3-pyridinecarboxylic acid and *i*-nic = 4-pyridinecarboxylic acid. The complexes were synthesized using a ruthenium blue solution as a precursor in the synthetic route, and characterized by electronic spectroscopy, vibrational FT-IR spectroscopy, and ¹H and ¹³C NMR. The results indicated a *trans* geometry. Cyclic voltammetry performed in water/acetone (1 : 1) solution revealed a *quasi*-reversible process centered on the Ru(II) species and a dependence of the redox potential, *E*_{1/2}, on the pH. The electronic spectra showed that the MLCT bands were also affected by the pH, undergoing a hypsochromic shift (blue shift) as the pH increased. The spectroelectrochemical analysis indicated that the bands in the visible region progressively faded as new UV bands emerged during the oxidation process. The equilibrium constants for *trans*-[RuCl₂(nic)₄] and *trans*-[RuCl₂(*i*-nic)₄] were determined by potentiometric titration, indicating that protonic species dominated at pH values lower than 2.6, whereas non-protonic species dominated at pH values higher than 5.0.

Keywords: Ruthenium(II) complex; electrochemistry; potentiometric titration

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INTRODUCTION

Coordination compounds containing ruthenium(II) as the metallic center have been extensively studied. Taube¹ and Wilkinson^{2,3} have investigated ruthenium complexes coordinated to amines, phosphines, pyridine and related ligands. Wilkinson *et al.*^{2,3} have shown that ruthenium blue solutions can be very effective in the preparation of a variety of complexes with general formula *trans*-[RuX₂(L)₄], where X is a halogen, and L is a monodentate ligand. The properties of such compounds can be tailored following an appropriate choice of the ligand, granting the complex potential for multiple applications. For instance, our group has recently presented a four-site ligand complex capable of undergoing electro-oxidative polymerization on the surface of the electrode.^{4,5} In addition, Reedijk *et al.*⁶ have studied the antitumoral properties of *trans*-[RuCl₂(dmsO)₄] (dmsO = dimethylsulfoxide) and [Him][*trans*-RuCl₄(Him)₂] (Him = imidazole). The synthesis of ruthenium complexes, even those partially soluble in water, is a challenging but promising task in the chemistry of ruthenium. It has been established that aqueous ruthenium can provide therapeutical action and that water soluble ruthenium complexes can be used as scavengers for nitric oxide in biological systems, also demonstrating a potential therapeutical value⁷ which has been recently established.⁸⁻¹⁰ In order to appraise the properties of this family of compounds, new ruthenium complexes have been synthesized using nic and *i*-nic ligands, where nic = 3-pyridinecarboxylic acid or nicotinic acid and *i*-nic = 4-pyridinecarboxylic acid or isonicotinic acid. The presence of carboxylic groups significantly increases the solubility of these complexes in water. This work contains details on the synthesis as well as spectroscopical and electrochemical characterization of new ruthenium complexes containing ligands originated from pyridinecarboxylic acids, in particular *trans*-[RuCl₂(nic)₄] (I) and *trans*-[RuCl₂(*i*-nic)₄] (II). Figure 1 illustrates the proposed structures for both complexes (I) and (II). The electrochemical and spectroelectrochemical experiments indicated that such compounds can be stored in water/acetone solution for times longer than the test span itself. Potentiometric studies were also conducted in order to select the most suitable conditions for coordinating divalent cations like Cu²⁺ and Ni²⁺ on the carboxylate group of nic and *i*-nic ligands. Our interest reside in investigation of the intramolecular redox reaction between the divalent cations and the ruthenium center. Such complexes can also be used in the catalysis of outer-sphere reactions.¹¹

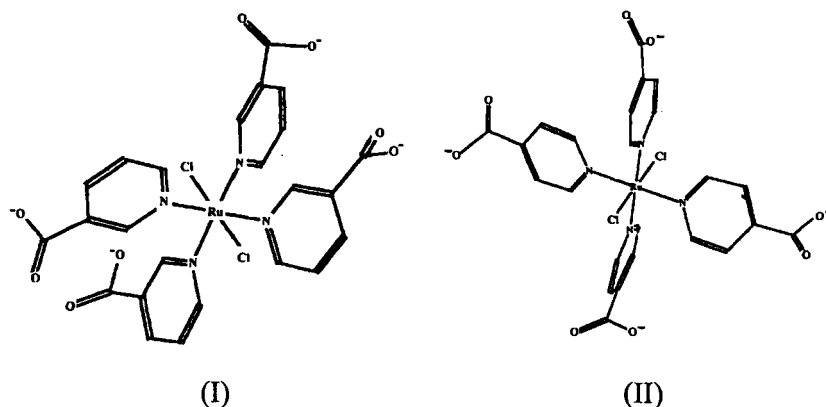


FIGURE 1 Suggested structures for complexes (I) and (II).

EXPERIMENTAL

Synthesis

Preparation of trans-[RuCl₂(nic)₄] (I)

The general steps followed in the preparation of *trans*-[RuCl₂(nic)₄] can be found in the literature.¹² A few modifications to the original procedure were implemented and are discussed below. A blue ruthenium solution was prepared from 260 mg (1.0 mmol) of RuCl₃·3H₂O to which 984 mg (8.0 mmol) of 3-pyridinecarboxylic acid were added. The system was refluxed for about 40 min under argon and vigorously stirred. The reaction progress was monitored by TLC and UV-vis spectroscopy. The reaction medium was then cooled for 12 h and vacuum filtered to eliminate any excess ligand. Next, the liquid was collected and moved to a separation funnel. Ethyl ether was then added to the point where two phases could be distinguished. A small volume of acetone could also be added to improve the solubility of the complex in the ethereal phase, thus improving the efficiency of extraction. The system was then vigorously stirred and the complex transferred to the ethereal phase. Subsequently, the organic phase was collected and the extraction steps repeated until all the product could be extracted. Finally, the organic phase was concentrated in vacuum and the amorphous complex was obtained. Whenever necessary, the product could be redissolved in water/acetone for another extraction. Yield 49.6% based on a starting value of RuCl₃·H₂O. *Anal. Calc.* for RuCl₂C₂₄H₂₀N₄O₈: C, 43.38; H, 3.03; N, 8.43.

Found: C, 43.62; H, 3.14; N, 8.42%. UV-vis λ_{\max} at pH 5.6 = 397 nm. IR 752 cm^{-1} (ν C-H); 934 cm^{-1} (ν OH); 1420 cm^{-1} (ν C-O-H); 1712 cm^{-1} (ν C=O); 3520 cm^{-1} (ν O-H). NMR ^1H : d (ppm) 9.3 (H_2 , H-Ar, m); 8.7 (H_6 , H-Ar, m); 8.3 (H_4 , H-Ar, d, 9 Hz); 7.4 (H_5 , H-Ar, m); NMR ^{13}C : d (ppm) 165 (C, -COOH); 151 (C_6 , Ar); 148 (C_2 , Ar); 140 (C_5 , Ar); 138 (C_4 , Ar); 125 (C_3 , Ar).

Preparation of trans-[RuCl₂(i-nic)₄] (II)

Complex (II) was prepared and purified in a similar way to that followed for complex (I), however, the ligand used was 4-pyridinecarboxylic acid. On occasion, a black tar was noticed during concentration of the organic phase. In this case, the product was redissolved in water and a second extraction with ethyl ether was necessary. The organic phase was then evaporated and the final product collected. This procedure was repeated until a reddish solid was obtained. Yield 43.5% based on a starting value of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$. *Anal. Calc.* for $\text{RuCl}_2\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_8$: C, 43.38; H, 3.03; N, 8.43. Found: C, 43.57; H, 3.10; N, 8.53%. UV-vis λ_{\max} at pH 5.6 = 421 nm. IR 768 cm^{-1} (ν C-H); 914 cm^{-1} (ν OH); 1416 cm^{-1} (ν C-O-H); 1712 cm^{-1} (ν C=O); 3588 cm^{-1} (ν O-H). NMR ^1H : d (ppm) 8.73 (2H_2 , H-Ar, dd, 2 and 8 Hz); 7.62 (2H_3 , H-Ar, dd, 1.5 and 8 Hz); NMR ^{13}C : d (ppm) 159.5 (1C, COOH); 137 (C_4 , Ar); 132 (C_2 , Ar); 129 (C_6 , Ar); 123 (C_3 and C_5 , Ar).

Reagents

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Johnson & Matthey) and ligands (Merck & Aldrich) were used with no previous purification. Commercially available solvents of analytical grade were used throughout the work. Spectroscopic and electrochemical analyses employed specific solvents, i.e., those with spectroscopic and chromatographic grade, respectively. Lithium perchlorate (Aldrich) was also used with no previous purification. Ultrapure argon (White-Martins) was used to provide the inert atmosphere necessary for data collection.

Experimental Apparatus

The electronic spectra were obtained using either a HP-8452 or an Aminco DW-2000TM spectrophotometer, equipped with quartz cuvettes of 1.0 cm optical path. ^1H and ^{13}C NMR spectra were obtained in $(\text{CD}_3)_2\text{CO}$ using a Bruker AC200F spectrometer. The vibrational spectra were measured using KBr pellets in a Perkin-Elmer 1GPC FT-IR system. Both the electrochemical and spectroelectrochemical measurements along with the corresponding experimental setup have been described in previous

publications.^{9,10} Data were collected using a typical three-electrode electrochemical cell. The auxiliary electrode was a platinum wire or sheet. The reference electrode consisted of Ag/AgNO₃ 0.1 mol·dm⁻³ in CH₃CN, and the working electrode was a platinum disk (0.115 cm²) previously polished to a 0.25 μm finish with alumina slurry. The electronic *iR* compensator of the equipment and a Luggin's capillary were used to perform *iR* corrections. Electrochemical data were collected for several pH solutions using water/acetone 1:1 and lithium perchlorate 0.1 mol·dm⁻³ solutions. The pH values were monitored *in situ* using a Cole-Parmer pH-meter. Acid media were prepared using HClO₄ and basic media using KOH 0.1 mol·dm⁻³.

Electronic Spectroscopy

Electronic spectra were obtained at several pH values using water/acetone (1:1 v/v) solution. Acid media were prepared using HCl 0.1 mol·dm⁻³ and basic media using NaOH 0.1 mol·dm⁻³. The pH values were measured using a digital Cole-Parmer 5986-60 pH-meter and data were collected in an Aminco DW-2000TM spectrophotometer.

Potentiometric Equilibrium Measurements

A potentiometric study of complexes (I) and (II) was carried out using a Micronal B-375 pH-meter equipped with a blue-glass electrode and a Ag/AgCl reference electrode calibrated with a standard HCl solution in acetone/water 1:1. With this procedure, $-\log[\text{H}^+]$ values were readily obtained. The electrode was calibrated using data obtained from potentiometric titration of a known volume of a standard 0.01 M HCl solution in acetone/water 1:1 v/v with a 0.1 M KOH standard. Samples containing about 0.050 mmol of ruthenium complex were individually dissolved in 50.0 mL of acetone/water 1:1 solution. They were then placed in a sealed thermostatic vessel at $25.00 \pm 0.05^\circ\text{C}$; complexes were adjusted to 0.1 M ionic strength by adding KCl, and therefore, water/acetone 1:1 v/v solution was chosen as the medium for potentiometric, electrochemical and spectrophotometric investigation.

RESULTS AND DISCUSSION

Electronic Spectroscopy

No significant difference was observed between the profiles corresponding to complex (I) and (II), as compared to those of *trans*-[RuCl₂(py)₄]³⁺ and

TABLE I Electronic spectroscopy data for complexes (I) and (II) in binary water/acetone 1:1 v/v solution as a function of the pH

| Complex | λ (nm) (ϵ) | | |
|---------|-------------------------------|-----------------|-----------------|
| | pH 3.0 | pH 5.6 | pH 12.0 |
| (I) | 399.7 (9209.3) | 397.3 (11807.3) | 395.4 (10465.2) |
| (II) | 445.5 (15770.2) | 421.2 (15448.4) | 416.0 (17109.5) |

trans-[RuCl₂(pmp)₄] complexes.⁴ Complex (I) revealed a very intense band at 406 nm and a second, less intense shoulder at 470 nm. Complex (II) showed a spectral characteristic similar to that found for complex (I), with λ_{\max} at 446 nm, in addition to a less intense shoulder at 520 nm. The bathochromic shift observed for complex (II) could be attributed to an effect arising from the presence of a carboxylic group in position 4 of the pyridinic ring. It alters the electron density on the nitrogen atom and, consequently, affects the metal–ligand interaction. The relationship between λ_{\max} and pH has also been investigated. Table I shows the λ_{\max} shift corresponding to complex (I) and (II) as a function of pH. For both complexes, a hypsochromic shift of the absorption bands was noticed as the pH increased. Such an effect was more representative for complex (II), displaying a 30 nm shift for variation in pH from 3.0 to 12.0. It could then be inferred that the electronic transitions were influenced not only by the position, but also by the degree of protonation, of the group present on the pyridine ring. Such a behavior can be explained based on crystal field theory. For the same compounds, no significant dependence of the value of ϵ on the pH has been observed.

Potentiometric Titration

Potentiometric titration assisted in the calculation of equilibrium constants corresponding to the development of species arising from an increase in protonation of the complexes. This increase in protonation was related to the carboxylic group present in the pyridinic ring. The values for protonation constants (Table II) were calculated using the BEST7 program¹⁶ and equation

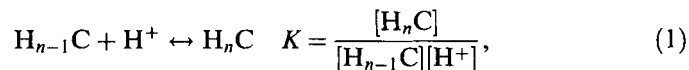


TABLE II Logarithms of protonation constants for *trans*-[RuCl₂(nic)₄] and *trans*-RuCl₂(*i*-nic)₄] at 25°C and $\mu = 0.1$ M KCl

| Species | <i>trans</i> -[RuCl ₂ (nic) ₄] | | | <i>trans</i> -[RuCl ₂ (<i>i</i> -nic) ₄] | | |
|-----------------|---|-------------------|-------|--|-------------------|-------|
| | % max | pH _{max} | log K | % max | pH _{max} | log K |
| Monoprotonated | 37.2 | 4.5 | 4.61 | 45.0 | 4.6 | 4.80 |
| Diprotonated | 56.3 | 3.9 | 4.42 | 47.0 | 4.0 | 4.31 |
| Triprotonated | 54.0 | 3.1 | 3.49 | 58.0 | 3.2 | 3.73 |
| Tetraprotonated | 83.7 | 2.0 | 2.72 | 86.1 | 2.0 | 2.80 |

where C refers to the proton-depleted complex. Titration curves corresponding to complexes (I) and (II) can be seen in Figures 2(a) and (b). The pH measurements were made as KOH was added to the system in small increments. Each titration was performed in such a manner as to collect 10–11 equally spaced points per equivalent of base added. The complexes had a long buffered region where the medium was acid and an inflection at $a = 4$, indicating the neutralization of 4 moles of protons per mol of the complex, where $a =$ mmoles of base/mmoles of the complex.

Figure 3 shows the distribution of species originating from complex (I) as a function of pH. Species C, which contains no protons, was the only species present at pH values higher than 5.0. The species containing one proton, HC, developed preferentially at a pH of 4.5, at which point it reached 37.02% of the total (I) concentration. H₂C, with two protons, had its maximum (56.3%) at a pH of 3.9, whereas the species with three protons had a maximum of 54.0% at a pH equal to 3.1. Finally, the species containing four protons dominated at pHs lower than 2.6. Figure 4 shows all the species related to complex (II) as a function of pH. Above a pH of 4.7 the species with no protons dominated, and above 7.0 it was the only one present. Species with one, two, three, and four protons had maxima at pH values lower than 5.0, 4.6 for the species with one proton, 4.0 for the one with two protons, 3.2 for three protons and 2.0 for four protons, and maxima of 45.0%, 47.0%, 58.0% and 86.1%, respectively. No significant change was observed in the values of the equilibrium constants of complex (I) and (II).

Electrochemistry and Spectroelectrochemistry

Cyclic voltammograms obtained in the range of -0.2 to 0.3 V vs. Ag/Ag⁺ revealed only one redox process centered in the metal, corresponding to the

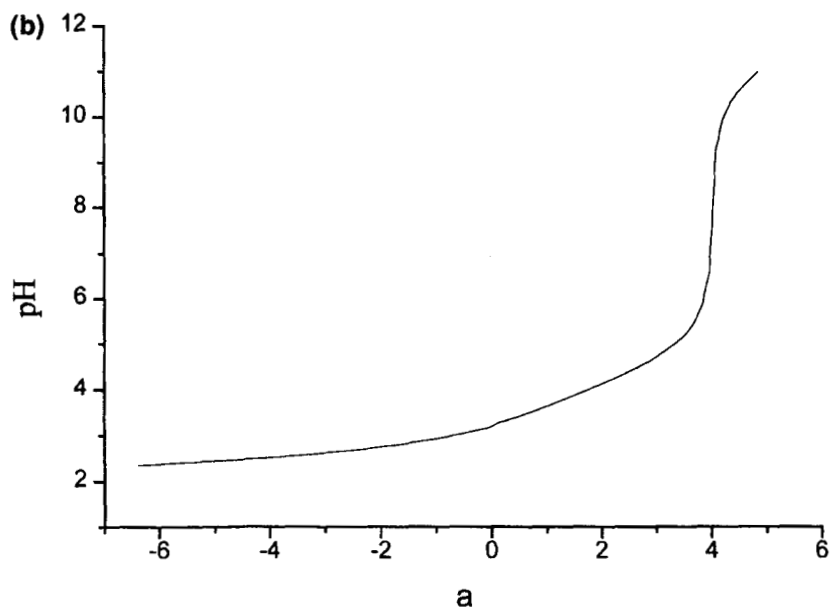
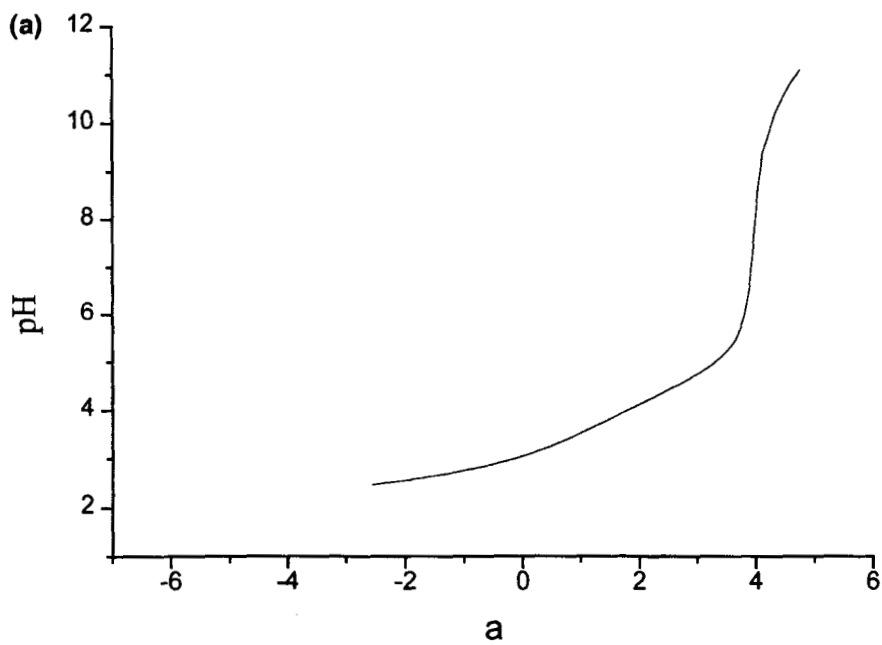


FIGURE 2 Experimental values of potentiometric titration on compound (a) (I) and (b) (II).

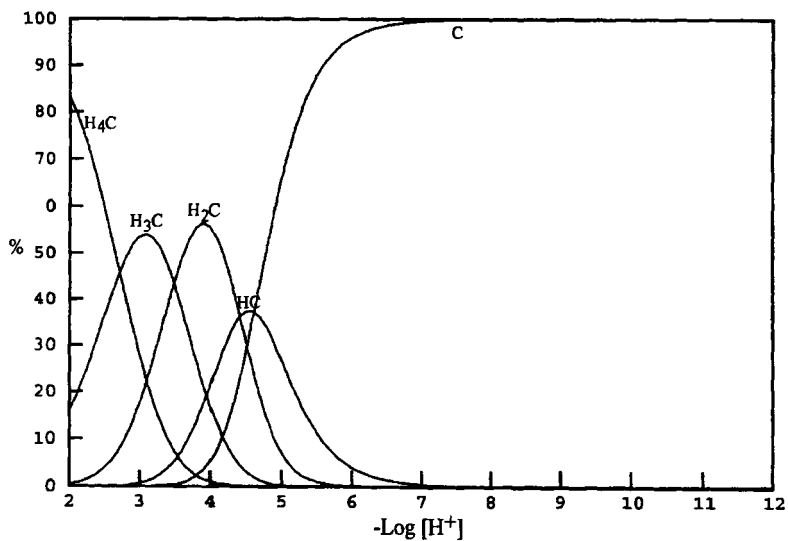


FIGURE 3 Distribution of protonic species corresponding to (I) as a function of the pH for binary water/acetone 1:1 system.

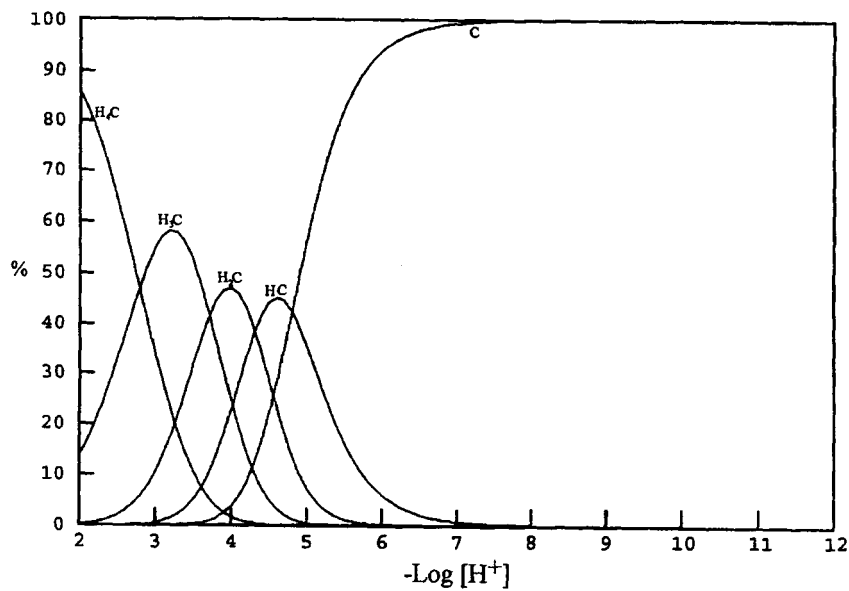


FIGURE 4 Distribution of protonic species corresponding to (II) as a function of the pH for binary water/acetone 1:1 system.

TABLE III Cyclic voltammetric data for the first oxidation process of *trans*-[RuCl₂(L)₄] (water/acetone 1 : 1 v/v, 25°C). Values for various pH values using a Pt working electrode and 100 mV·s⁻¹ scan rate

| pH | <i>trans</i> -[RuCl ₂ (nic) ₄] | | | <i>trans</i> -[RuCl ₂ (i-nic) ₄] | | |
|------|---|------------------------------|---|---|------------------------------|---|
| | <i>E</i> _{1/2} (mV) ^a | Δ <i>E</i> _p (mV) | <i>i</i> _{pa} / <i>i</i> _{pc} | <i>E</i> _{1/2} (mV) ^a | Δ <i>E</i> _p (mV) | <i>i</i> _{pa} / <i>i</i> _{pc} |
| 2.20 | 67.4 | 76.6 | 1.011 | 111.6 | 78.9 | 1.440 |
| 2.45 | 72.5 | 77.5 | 0.963 | 111.1 | 76.6 | 1.430 |
| 2.75 | 68.5 | 77.6 | 1.009 | 109.1 | 77.2 | 1.421 |
| 3.05 | 71.6 | 80.7 | 1.017 | 106.5 | 77.0 | 1.410 |
| 3.40 | 70.6 | 77.6 | 0.979 | 103.6 | 76.8 | 1.400 |
| 4.42 | 50.3 | 84.4 | 0.950 | 66.2 | 83.0 | 1.330 |
| 5.40 | -15.8 | 85.7 | 1.013 | -13.4 | 86.3 | 1.220 |
| 6.35 | -33.7 | 91.1 | 0.966 | -24.6 | 83.5 | 1.130 |
| 9.57 | — | — | — | -24.0 | 91.0 | 1.190 |

^aReference electrode Ag/Ag⁺.

trans-[RuCl₂(L)₄]^{3+/2+} couple. Table III shows the results for the main electrochemical parameters obtained for complexes (I) and (II) at different pH levels. The Δ*E*_p values were rather similar, slightly increasing with pH. The separation between peak potential values, Δ*E*_p, suggested a *quasi*-reversible process. The *i*_{pa}/*i*_{pc} ratio was close to one throughout the entire pH range investigated for complex (I), whereas that value exceeded one for complex (II) in the same pH range. The reasons for such a discrepancy remains unknown. Figures 5(a) and (b) depict the voltammetric profiles obtained from complexes (I) and (II), respectively, for different pH values. As for the position of λ_{max}, both compounds showed a strong dependence of *E*_{1/2} on the pH of the solution. A shift of *E*_{1/2} towards cathodic potentials takes place as the pH increases, confirming the electronic spectroscopy measurements. Table III shows a clear relationship between *E*_{1/2} and the pH for complexes (I) and (II). In the pH range from 2.20 to 6.35, the variation of *E*_{1/2} reached 101 mV for complex (I), and 135.6 mV for complex (II). Similar to what was observed from UV-vis results, an increase in the pH significantly affects *E*_{1/2} of complex (II) as compared to complex (I). The correlation between *E*_{1/2} and the pH can be attributed to variation in the electron density of the ligand as the complexes lose their protons. The voltammetric profiles of complex (II) showed a current level above the background, at both ends of the potential sweep. A similar behavior was observed by Bond and Haga¹⁷ during a voltammetric study of ruthenium complexes containing bis(2,2'-bipyridine)(2,2'-bibenzimidazole) ligands in acetonitrile-water mixtures.

The results of the potentiometric titration assisted in interpretation of the electrochemical data. From Figure 6, it can be seen that up to pH 6.0, *E*_{1/2}

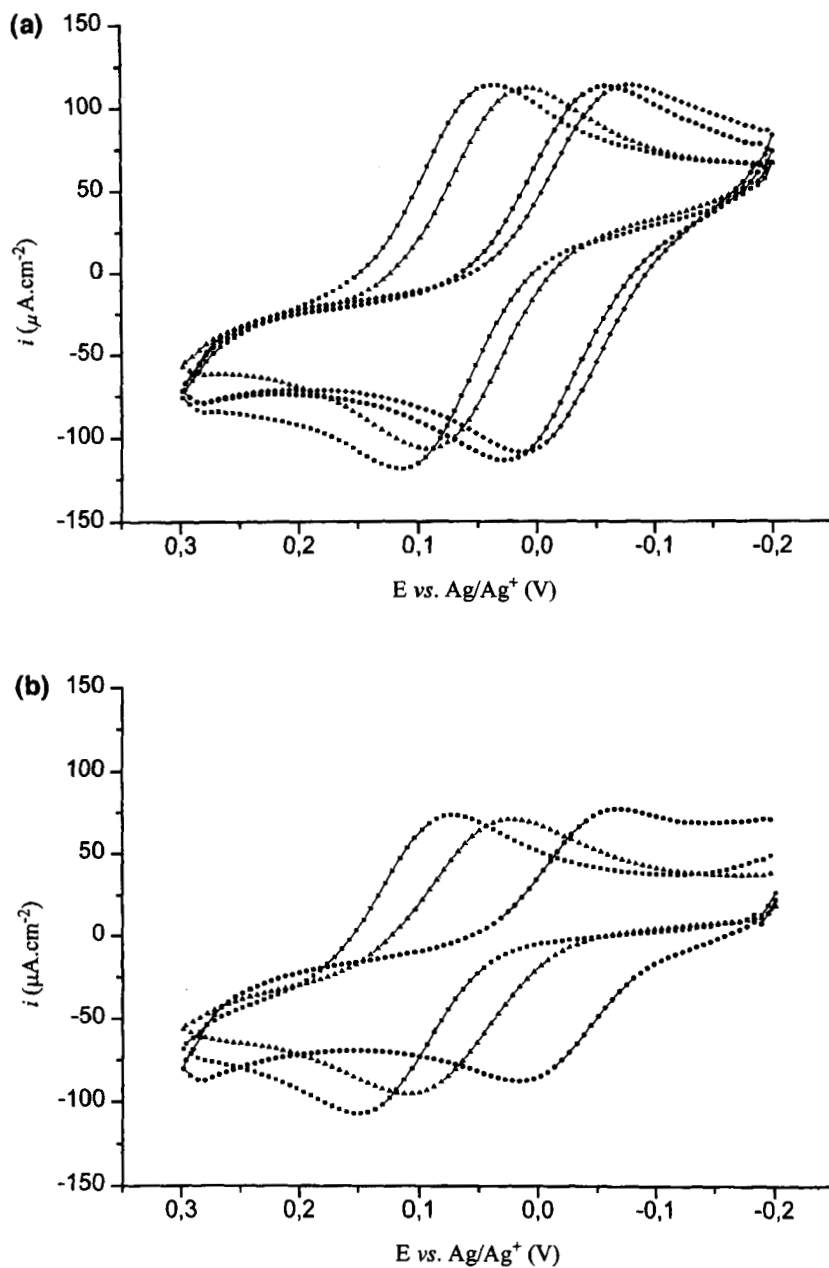


FIGURE 5 Cyclic voltammograms obtained for different pH values. (a) (I), pH: 1.86(—■—), 4.42(—▲—), 5.46(—●—), and 6.40(—◆—); (b) (II), pH: 2.21(—■—), 4.37(—▲—), and 6.25(—●—). Data gathered in a binary water/acetone 1:1 system - LiClO_4 $0.1 \text{ mol}\cdot\text{dm}^{-3}$, using a Pt-electrode and $100 \text{ mV}\cdot\text{s}^{-1}$ scan rate.

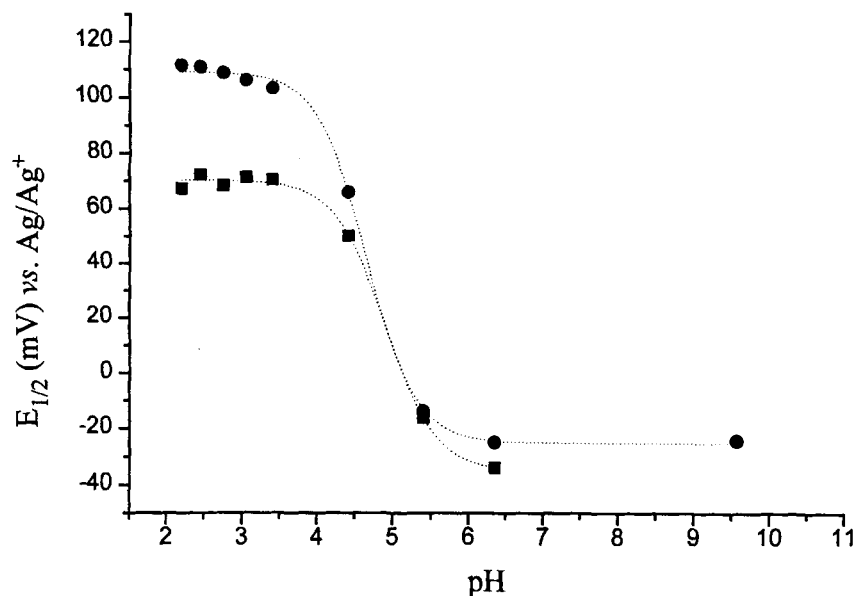


FIGURE 6 Comparative view of dependence of $E_{1/2}$ for (I)(■) and (II)(●) complexes as a function of the pH.

decreases as the pH increases. From that point on, $E_{1/2}$ is constant, consistent with the potentiometric result that showed a species with no protons dominating at pH values higher than 5.0 (Figures 2(a) and (b)). Therefore, $E_{1/2}$ is constant in a medium containing only one species, but varies if more than one species is present.

Spectroelectrochemical analysis was carried out for complexes (I) and (II). Regardless of the pH value, for both complexes as the main band faded, a new higher energy band emerged. Figure 7 depicts the oxidation of complex (II) in water/acetone 1:1 solution at a pH of 9.8. The spectra were obtained in the potential range from -0.40 to 0.40 V vs. Ag/Ag⁺. As the 416 nm band fades, a new band is formed towards the UV region, with an isobestic point at 350 nm. The isobestic points and the main bands underwent similar hypsochromic shifts, as the pH values increased. For instance, the isobestic points for complex (II) were found at 372, 355, and 350 nm corresponding to pH values of 1.73, 4.90, and 9.83, respectively. Both complexes showed high stability, as the spectra of the reduced species were completely restored when an E_{applied} of -0.40 V vs. Ag/Ag⁺ was applied to complexes (I) and (II). The slope of the E_{applied} vs. $\log([O]/[R])$ plots was

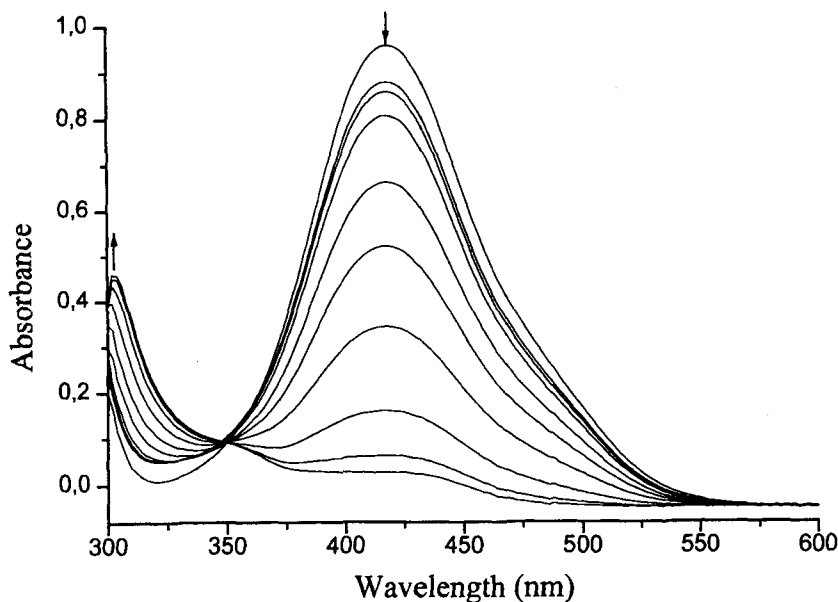


FIGURE 7 Superimposed electronic spectra characteristic of the oxidation of *trans*-[RuCl₂(*i*-nic)₄] for different potentials. Data obtained in Optically Transparent Electrode (OTE) and water/acetone 1 : 1 (pH = 9.8).

around 59 mV, which is typical for a transfer process involving one electron. Pulse differential voltammetric analyses resulted in a FWHH (full width at half height) factor close to 90 mV, suggesting a value of $n \approx 1$. In addition, values of $E_{1/2}$, calculated from the intersection points of the curve, were compatible with the results obtained from cyclic voltammetry.

CONCLUSIONS

The *trans*-[RuCl₂(nic)₄] (I) and *trans*-[RuCl₂(*i*-nic)₄] (II) complexes were characterized by CHN elemental analysis, UV-vis, ¹H and ¹³C NMR, cyclic voltammetry and potentiometry. The species distributions of these systems make possible the selection of the most suitable conditions for coordination of Cu²⁺ and Ni²⁺ on the carboxylate group on the ligands *i*-nic and nic, allowing us to study the intramolecular electron transfer reactions between these divalent cations and the central Ru²⁺ metal. Results of titration with these divalent metals and their redox reaction will be

described in a subsequent publication. Correlation between results from potentiometric titration and cyclic voltammetry titration are also established.

References

- [1] D.W. Raichart and H. Taube, *Inorg. Chem.*, **11**, 999 (1972).
- [2] E.W. Abel, M.A. Bennett and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).
- [3] J.D. Gilbert, D. Rose and G. Wilkinson, *J. Chem. Soc. A*, 2765 (1970).
- [4] M.M.S. Paula and C.V. Franco, *J. Coord. Chem.*, **40**, 71 (1996).
- [5] M.M.S. Paula, C.V. Franco, P.B. Prates and V.N. de Moraes Jr., *Synthetic Metals*, **90**, 81–88 (1997).
- [6] M. Heijden, P.M. van Vliet, J.G. Haasnoot and J. Reedijk, *J. Chem. Soc. Dalton Trans.*, 3675 (1991).
- [7] M.J. Abrams, 31st International Conference on Coordination Chemistry, Vancouver. *Abstracts*, pp. 8, 18–23 (1996).
- [8] C.V. Franco, M.M. Meier, M.M.S. Paula, A. Beirith, T.B. Creczynski-Pasa and J.B. Calixto, *Journal of Inorganic Biochemistry*, **67** (1–4), 144 (1997).
- [9] T.B. Creczynski-Pasa, V.R. Boneti, A. Beirith, K. Ckless, M.M. Meyer, M.M.S. Paula, C.V. Franco and J.B. Calixto "Ruthenium complex at its biological effects as anti-noceptione via Nitric Oxide pathway, and as free radical scavenger", in preparation, to be submitted to *Molecular Pharmacology*.
- [10] C.V. Franco, M.M.S. Paula, B. Szpoganicz and M.M. Meier, "An electrochemical study of biologically-active ruthenium (II) complexes" 32nd International Conference on Coordination Chemistry, Chile, *Abstracts 2P2*, p. 32 (1997).
- [11] Y.-T. Fanchiang, R.R. Carlson, P.K. Thamburaj and Edwin S. Gould, *J. Am. Chem. Soc.*, **99**(4), 1073–1077 (1977).
- [12] F. Bottomley and M. Mukaida, *J. Chem. Soc. Dalton Trans.*, 1933 (1982).
- [13] M.M.S. Paula and C.V. Franco, *Quimica Nova*, **17**(5) (1994).
- [14] M.M.S. Paula and C.V. Franco, *Coord. Chem.*, **36**, 247 (1995).
- [15] C.V. Franco, V.N. de Moraes Jr., F. Mocellin and M.M.S. Paula. *J. Mater. Chem.*, (in press).
- [16] A.E. Martell and R.J. Motekaitis, *Determination and Use of Stability Constants*, VCH (New York, 1975).
- [17] A.M. Bond and M. Haga, *Inorg. Chem.*, **25**, 4507–4514 (1986).