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Synthesis and characterization of a new ruthenium (II) terpyridyl diphosphine complex

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ABSTRACT. Ruthenium complexes have been prepared for several applications, mostly for electrocatalysis, catalytic hydrogenation, energy conversion, photolysis, medicinal chemistry, among other fields. Bipyridine and terpyridine ligands are commonly found in the metal coordination sphere, including ruthenium, largely due to the high stability exhibited by the resulting complex and the possibility of greater stereochemical control during synthesis. The combination of substituted terpyridine ligands with diphosphine ligands to the metal ruthenium occurs to a lesser extent and its catalytic potential has been examined in several studies. This paper describes the synthesis of a new ruthenium (II) aqua complex containing aryl diphosphine and substituted terpyridine ligands: $[Ru(L)(totpy)(OH_2)](ClO_4)_2$ *($L=Ph_2PCH_2CH_2PPh_2$); (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine)*. The synthesis route was conducted in three steps; the final and the intermediate products have shown good reaction yields; the results of the characterization of the aqua complex by cyclic voltammetry, UV-visible spectroscopy and elemental analysis are consistent with the proposed chemical structure.

Keywords: diphosphine; metal complex; ruthenium.

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Introduction

Ruthenium complexes (Ru, atomic number 44; atomic mass 101.1), tend to exhibit remarkable stability. Ruthenium can combine with numerous organic or non-organic ligands in synthetic routes that are generally reliable (Malecki, 2012).

Ruthenium complexes are applied in several areas of knowledge, depending on the chemical structure of the ligands. In recent years, they have been used in the structures of solar panels for energy conversion (Ameta & Ameta, 2016; Sadig & Nazeeruddin, 2018). They have also extended their use in medicine, and some authors consider ruthenium (II) complexes promising for the development of a new generation of antitumor drugs (Lin, Zhao, & Bo, 2018), because they offer advantages related to the platinum complexes commonly used in these types of treatment, such as greater efficacy and lower toxicity (Abid, Shamsi, & Azam, 2016; Thota, Rodrigues, & Crans, 2018). Studies have been carried out in order to use nanoparticulate systems for the development of drug potentially useful against cancer and also as biocatalysts (Zeng et al., 2017); polypyridine ruthenium complexes with chiral characteristics have been explored with significant activity against several types of cancer in *in vitro* tests (Wang et al., 2014).

Ruthenium complexes have played important role as catalysts in reactions, in which numerous types of important transformations are reported, e.g., in Belousov-Zhabotinsky oscillating chemical reactions (Delgado, Zhang, & Xu, 2011), in conversions of amines to nitriles (Cristian et al., 2013), and in hydrogenations (Van Ravensteijn, Schild, & Kegel, 2017).

The literature describes ruthenium complexes containing tridentate polypyridine ligands used for different purposes. These complexes exibt high stability with negligible tendency to lose ligands during the chemical processes (Meyer, 1984; Tse et al., 2005; Ezhilarasu, Sathiyaseelan, & Kalaichelvan, 2017).

Ruthenium complexes containing diphosphine ligands have been reported since 1978 (Sullivan, Salmon, & Meyer, 1978). However, less frequent is the combination of polypyridine and diphosphine ligands (Dovletoglou, Adeyemi, & Meyer, 1996; Sussuchi, Lima, & De Giovani, 2006; Almeida et al., 2014; Mello-Andrade et al., 2018). This may be due to the complexity of the preparation of polypyridine ligands, especially substituted terpyridines (Hanabusa, Nakamura, & Koyama, 1994; Ezhilarasu et al., 2017). Bidentate diphosphine ligands offer some advantages related to their phosphine analogues by providing better control of the stereochemistry of the resulting complex and by decreasing ligand exchange processes (Chaudret, Delavaux, & Poilblanc, 1988; Gao, Wan, & Wong, 1996).

Our research group has carried out systematic electrocatalytic studies in a series of organic substrates, using ruthenium polypyridine aqua/oxocomplex systems containing phosphine or arsine ligands and the results have shown that these complexes are more selective than those containing polypyridine ligands only (Sussuchi, Lima, & De Giovani, 2006; Batalini & De Giovani, 2020). In this work we have synthesized a new ruthenium terpyridyl diphosphine aqua complex: [Ru(L)(totpy)(OH_2)](ClO_4)$_2$ *(L=$Ph_2PCH_2CH_2PPh_2$); (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine)* (Figure 1); the complex was characterized by elemental analysis, cyclic voltammetry and UV-visible spectroscopy.

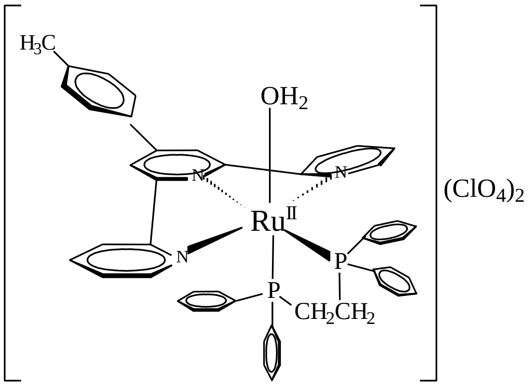

Figure 1. Structure of [Ru(L)(totpy)(OH_2)](ClO_4) *(L=$Ph_2PCH_2CH_2PPh_2$); (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine).*

Material and methods

Materials and reagents

Water was doubly distilled from alkaline potassium permanganate (Morita & Assumpção, 2007). Diethyl ether was previously dried by keeping it over anhydrous $MgSO_4$, distilled and subsequently dried over metallic sodium and redistilled (Morita & Assumpção, 2007). Methylene chloride was dried in an alumina column. All other reagents and solvents were PA grade (Merck, Aldrich, Mallinckrodt, Sigma) and were used without further purification. The pH 8.1 solution was 7:3 phosphate buffer (NaH_2PO_4/$Na_2HPO_4.H_2O$), (μ=0.25 mol.L^{-1}):tert-butyl alcohol). The pH values of the buffer:tert-butyl alcohol solutions were determined from direct pH meter readings and are therefore apparent pH values. Tetrabutylammonium perchlorate (TBAP) was prepared from tetrabutylammonium bromide, according to a classic literature procedure (Sawyer & Roberts, 1974).

Instrumentation and measurements

Electrochemical experiments were carried out at room temperature and pressure, in a FAC-200A potentiostat/galvanostat coupled to an Intralab current data logger. Cyclic voltammetric and differential voltammetric experiments were performed in a one-compartment glassy carbon working electrode (0.086 cm^2, 0.40 cm diameter), a platinum wire auxiliary electrode, and a saturated calomel electrode (SCE). ^{1}H NMR spectra were recorded in a Bruker AC-80 (80MHz) NMR spectrometer, using deuterated chloroform as solvent and tetramethylsilane as internal standard (0 ppm on the δ scale). UV-visible spectra were obtained in 1.00 cm quartz cells by using a 8452A Hewlett Packard diode array spectrophotometer. Elemental analyses were performed using a CNH Perkin Elmer Model 2400, at Institute of Chemistry of the University of São Paulo (USP). EPR spectra were obtained at -196°C in a Bruker ESP 300E EPR spectrometer.

Synthesis of the ligand *4’-(4-tolyl)-2,2’:6’,2”-terpyridine (totpy)*

The totpy ligand was prepared in three stages, analogously to literature procedures (Basset, 1981; Spahni, & Calzagerri, 1984; Constable, Ward, & Corr, 1988). The product was characterized by ^{1}H NMR spectrum. The details of each step of the synthesis have been recently published (Batalini & De Giovani, 2019).

Synthesis of the complex [Ru(L)(totpy)(OH_2)](ClO_4)$_2$ *(L=$Ph_2PCH_2CH_2PPh_2$) (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine)*

The synthesis of the complex [Ru(L)(totpy)(OH_2)](ClO_4)$_2$ involved three steps, as shown in Figure 2 and described below.

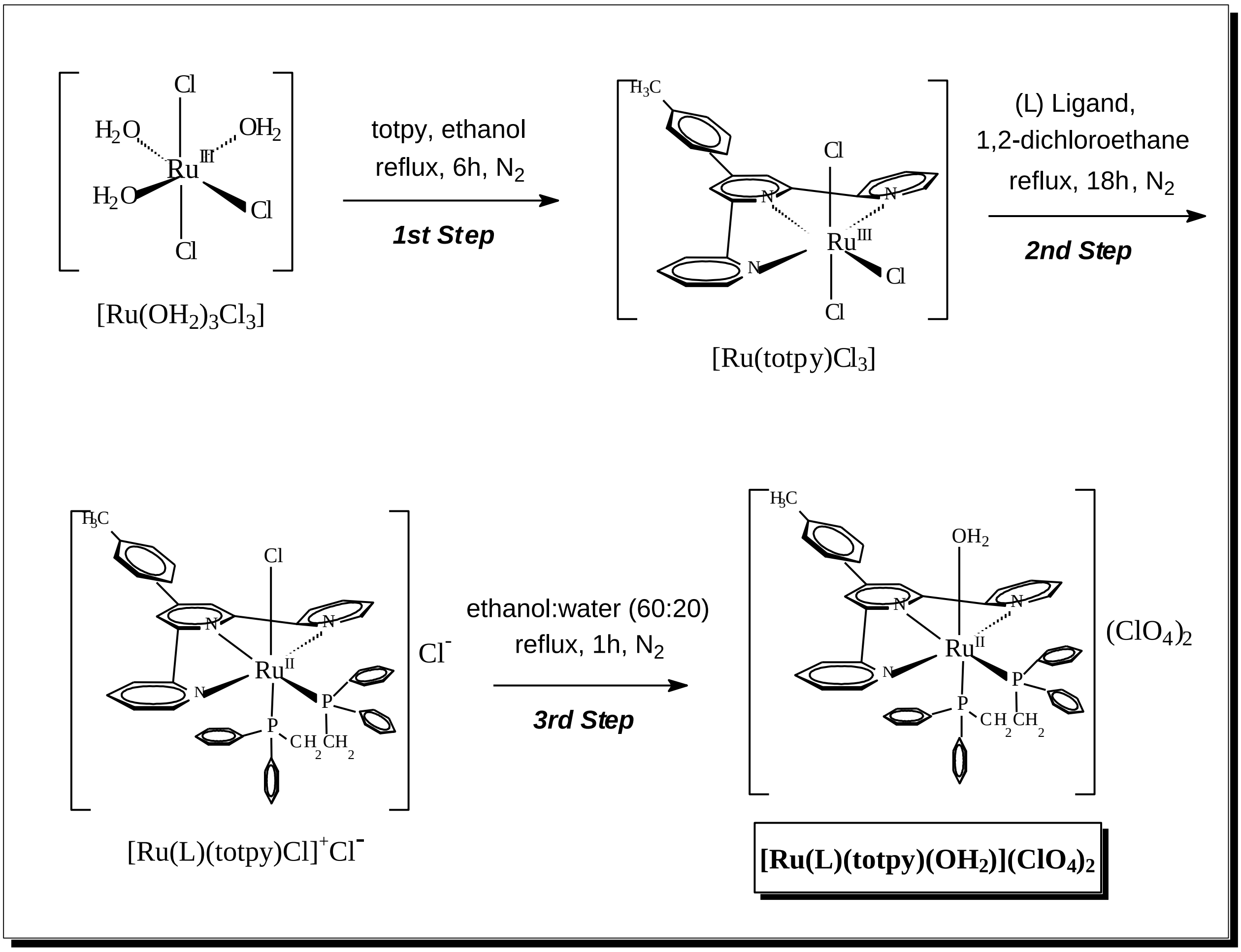

Figure 2. Synthesis of the complex [Ru(L)(totpy)(OH_2)](ClO_4) *(L=$Ph_2PCH_2CH_2PPh_2$); (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine).*

1st Step – Synthesis of the complex [Ru(totpy)Cl_3] *(totpy=4´-(4-tolyl)-2,2´:6´,2´´- terpyridine)* (Sullivan, Calvert, & Meyer, 1980):

A mixture of [Ru(OH_2)Cl_3] (0.46 g, 1.76 mmol) and totpy (0.57 g, 1.76 mmol) was kept under N_2 atmosphere, in 250 mL of ethanol, for 3.0 h. The mixture was then refluxed for 6.0h, under N_2. The solvent was evaporated to about 70 mL and the remaining solution was cooled to 0°C. The solution was filtered, the product was washed with diethyl ether and dried under vacuum. The complex was characterized by cyclic voltammetry, UV-visible spectroscopy and elemental analysis.

2nd Step – Synthesis of the complex [Ru(L)(totpy)Cl]$^+$Cl$^-$ *(L=$Ph_2PCH_2CH_2PPh_2$); (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine)*:

A mixture of [Ru(totpy)Cl_3] (0.40 g (0.75 mmol), 1,2-bisdiphenylphosphinoethane (L) (0.34 g (0.85 mmol), LiCl (0.10 g) and 0.5 mL of trimethylamine was refluxed, under N_2 atmosphere, in 200 mL of 1,2-dichloroethane, for 18 h. The solvent was evaporated to dryness. The product was recrystallized twice by dissolving it in 2 mL of $CHCl_3$ and precipitating by addition of 200 mL of diethyl ether. The solution was filtered and the crystals were dried under vacuum. The complex was characterized by cyclic voltammetry and UV-visible spectroscopy.

3rd Step – Synthesis of the complex [Ru(L)(totpy)(OH_2)](ClO_4)$_2$ *(L=$Ph_2PCH_2CH_2PPh_2$) (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine)*:

[Ru(L)(totpy)Cl]$^+$Cl$^-$ (0.40 g, 1.21 mmol) and silver p-toluenesulfonate (0.60 g, 2.00 mmol) were heated to reflux in 60:20 mL of ethanol:water, under N_2 atmosphere, for 1 h. The volume was reduced, the solution was cooled to room temperature and filtered to remove the AgCl. Then, 5 mL of a $NaClO_4$ saturated solution were added to the filtrate. The product was recrystallized by dissolving it in 2 mL of methylene chloride and precipitating it by dropping the solution on 200 mL of diethyl ether. The crystals were collected by filtration and dried under vacuum. The aqua complex was characterized by cyclic voltammetry, UV-visible spectroscopy and elemental analysis.

Results and discussion

Synthesis of the ligand *4'-(4-tolyl)-2,2':6',2''-terpyridine (totpy)*

The *totpy* ligand was characterized by ^{1}H NMR (δ, $CDCl_3$), showing the following signals: 8.50-8.80 (m, 6H); 7.70-8.00 (m, 4H); 7.15-7.40 (m, 4H); 2.40 (s, 3H). The signals are consistent with the chemical structure of terpyridine ligand, since only methyl hydrogens appear in a more shielded field and the remaining signals of aromatic hydrogens in a less shielded field (Batalini & De Giovani, 2019).

Synthesis of the complex $[Ru(L)(totpy)(OH_2)](ClO_4)_2$ *($L=Ph_2PCH_2CH_2PPh_2$) (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine)*

The synthesis of ruthenium (II) terpyridyl diphosphine aqua complex involved three steps as discussed below.

1st Step – Synthesis of the complex $[Ru(totpy)Cl_3]$ *(totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine)* (Sullivan, Calvert, & Meyer, 1980):

Brown crystals were obtained. Yield 0.72 g (78%). The cyclic voltammetric and UV-vis experiments were carried out in acetonitrile (Figures 3 and 4); the data, including those of elemental analysis are shown below and are consistent with those of the literature.

- UV-visible spectroscopy (Figure 3): $\lambda_{max.}$= 412 nm (ε= 8100 mol^{-1}.L.cm^{-1}); literature (Lima et al., 1998): $\lambda_{max.}$= 410 nm (ε= 7800 mol^{-1}.L.cm^{-1}).
- Cyclic voltammetry (Figure 4): $E_{1/2}$ = +0.01 V, corresponding to the Ru$^{IV/III}$ system; literature (Lima et al., 1998): $E_{1/2}$ = +0.01 V ($E_{1/2}$ = half-wave potential).
- Elemental analysis: *(theoretical values (%) / experimental values (%) / errors (%))*: C (49.82 / 49.34 / 1.00); H (3.23 / 3.32 / 2.80); N (7.92 / 7.51 / 5.00).

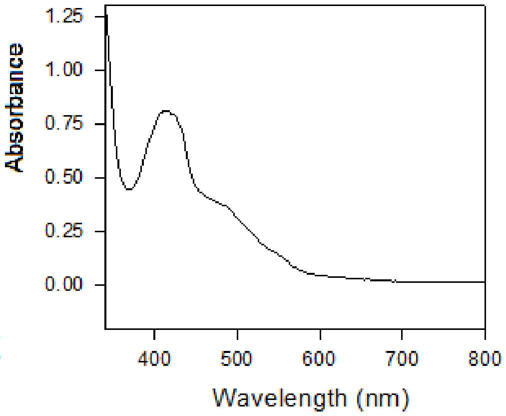

Figure 3. UV-vis spectrum of 0.10 mmol.L^{-1} $[Ru(totpy)Cl_3]$ *(totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine)*, in CH_3CN.

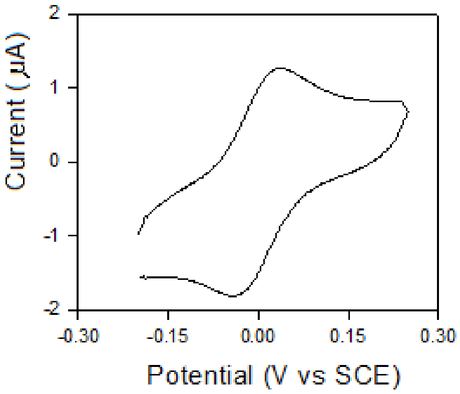

Figure 4. Cyclic voltammogram of 1.00 mmol.L^{-1} $[Ru(totpy)Cl_3]$ *(totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine)*, in CH_3CN + 0.1 mol.L^{-1} TBAP, at 0.10 V.s^{-1}, glassy carbon working electrode.

2nd Step – Synthesis of the complex $[Ru(L)(totpy)Cl]^+Cl$ *(L=$Ph_2PCH_2CH_2PPh_2$); (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine)*:

Purple crystals were obtained. Yield 0.57 g (85%). The UV-vis and cyclic voltammetric experiments were carried out in methylene chloride (Figures 5 and 6).

- UV-visible spectroscopy (Figure 5): $\lambda_{max.}$= 550 nm (ε= 2700 mol^{-1} L cm^{-1}).
- Cyclic voltammetry (Figure 6): $E_{1/2}$ = +0.49 V (corresponding to the $Ru^{III/II}$ system of a possible concomitant product) and $E_{1/2}$ = +1.12 V (corresponding to the $Ru^{III/II}$ system of the chloro complex).

In this step, the diphosphine ligand is related to the reduction process of ruthenium (III) to ruthenium (II); phosphorus act as electron back donor to the central metal, as verified in some works with similar complexes (Gericke & Wagler, 2017; Wu et al., 2017). The side bands observed in the UV-vis spectrum and two pairs of waves in the cyclic voltammogram indicate the presence of a concomitant product, probably the $[Ru(totpy)Cl_3]$ which may have not completely reacted. Attempts to purify the monochloro complex using a neutral Al_2O_3 column, eluting with different chloroform:methanol ratios were not successful. Albeit not completely pure, the purity of the monochloro complex was considered satisfactory as a starting material for the synthesis of the terpyridyl diphosphine aqua complex (step 3).

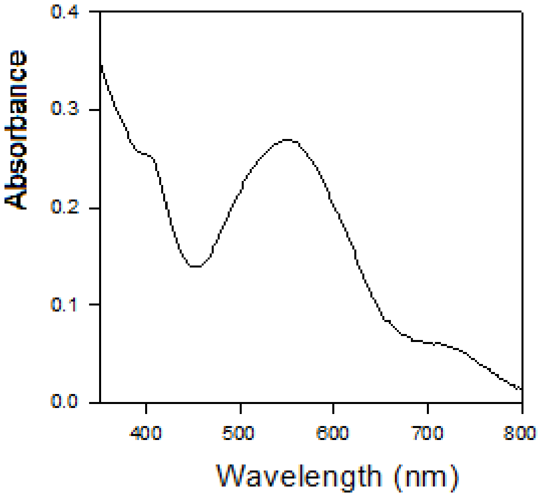

Figure 5. UV-vis spectrum of 0.10 $mmol.L^{-1}$ $[Ru(L)(totpy)Cl]^+Cl$ *(L=$Ph_2PCH_2CH_2PPh_2$); (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine)* in CH_2Cl_2.

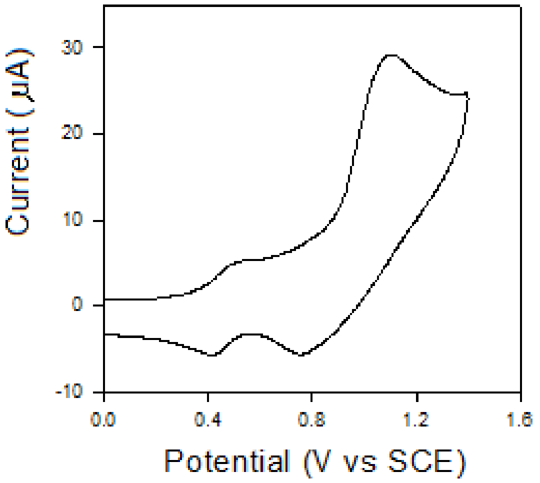

Figure 6. Cyclic voltammogram of 1.00 $mmol.L^{-1}$ $[Ru(L)(totpy)Cl]^+Cl$ *(L=$Ph_2PCH_2CH_2PPh_2$); (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine)* in CH_2Cl_2 + 0.1 $mol.L^{-1}$ TBAP, at 0.10 $V.s^{-1}$, glassy carbon working electrode.

3rd Step – Synthesis of the complex $[Ru(L)(totpy)(OH_2)](ClO_4)_2$ *(L=$Ph_2PCH_2CH_2PPh_2$); (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine)*:

Red crystals were obtained. Yield 0.31 g (66%). The elemental analysis data are shown in Table 1 and are consistent with the proposed formula.

Table 1. Elemental analysis data for the complex [Ru(L)(totpy)(OH_2)](ClO_4)$_2$ *(L=$Ph_2PCH_2CH_2PPh_2$); (totpy=4'-(4-tolyl)-2,2':6',2''-terpyridine*).

Elements	Calculated	Experimental	Error (%)
C (Carbon)	55.40	55.20	0.4
H (Hydrogen)	4.17	4.22	1.2
N (Nitrogen)	4.04	4.23	4.7

Table 2 summarizes the UV-vis spectroscopic and cyclic voltammetric data for the complex. Figures 7, 8, 9 and 10 show the UV-vis spectra and cyclic voltammograms of the aqua complex.

Table 2. Spectral and electrochemical data for the complex [Ru(L)(totpy)(OH_2)](ClO_4)$_2$ *(L=$Ph_2PCH_2CH_2PPh_2$); (totpy=4'-(4-tolyl)-2,2':6',2''-terpyridine)*.

UV-vis Spectroscopy		Cyclic Voltammetry	
$\lambda_{max.}$, *nm* (ε_{max} x 10^3, *mol^{-1}.L.cm^{-1}*)		$E_{1/2}$ *(V vs SCE)*	
CH_2Cl_2	pH 8.1 [1]	CH_2Cl_2 [2]	pH 8.1 [3]
448 (3.7)	444 (3.9)	+0,72, +0.97, +1.18 [4]	+0.37, +0.62 [4]
484 (3.8)	480 (3.7)	*+0.70,+0.95,+1.17* [5]	*+0.36,+0.62,+0.89* [5]

[1] 7:3 phosphate buffer: tert-butyl alcohol solution, pH 8.1; [2] CH_2Cl_2 + 0.10 mol.L^{-1} Bu_4NClO_4, ν=0.10 V.s^{-1}, glassy carbon working electrode; [3] 7:3 phosphate buffer: tert-butyl alcohol solution, pH 8.1, ν = 0.10 V.s^{-1}, glassy carbon working electrode; [4] Redox waves ($E_{1/2}$), obtained by cyclic voltammetry; [5] Anodic peak potentials (E_{pa}), obtained by differential pulse voltammetry.

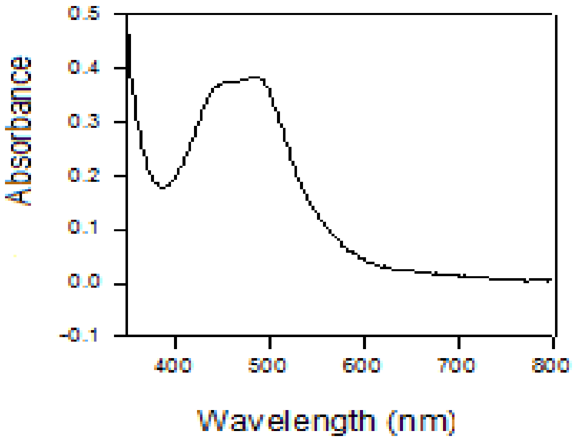

Figure 7. UV-vis spectrum of 0.10 mmol.L^{-1} [Ru(L)(totpy)(OH_2)](ClO_4)$_2$ (L=$Ph_2PCH_2CH_2PPh_2$); (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine), in CH_2Cl_2.

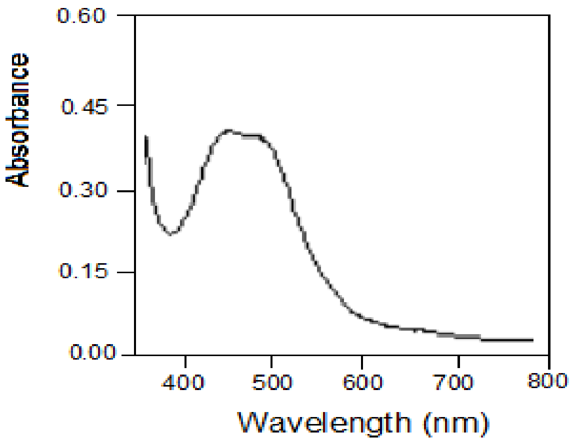

Figure 8. UV-vis spectrum of 0.10 mmol.L^{-1} [Ru(L)(totpy)(OH_2)](ClO_4)$_2$ (L=$Ph_2PCH_2CH_2PPh_2$); (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine) in 7:3 phosphate buffer:tert-butyl alcohol solution, pH 8.1.

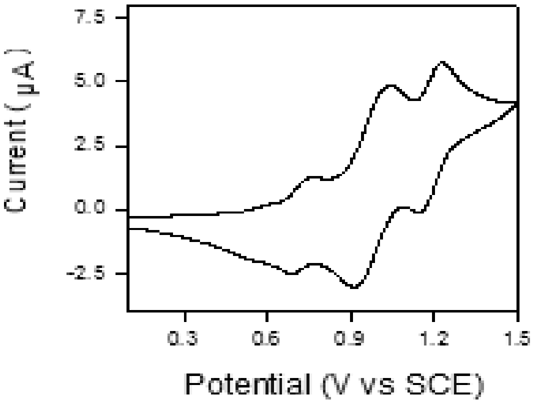

Figure 9. Cyclic voltammogram of 1.00 mmol.L^{-1} $[Ru(L)(totpy)(OH_2)](ClO_4)_2$ ($L=Ph_2PCH_2CH_2PPh_2$); (totpy=4′-(4-tolyl)-2,2′:6′,2′′-terpyridine) in CH_2Cl_2 + 0.1 mol. L^{-1} TBAP, at 0.10 $V.s^{-1}$, glassy carbon working electrode.

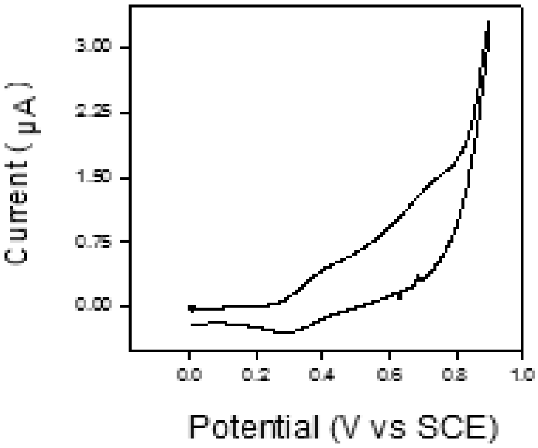

Figure 10. Cyclic voltammogram of 1.00 mmol.L^{-1} $[Ru(L)(totpy)(OH_2)](ClO_4)_2$ ($L=Ph_2PCH_2CH_2PPh_2$); (totpy=4′-(4-tolyl)-2,2′:6′,2′′-terpyridine) in 7:3 phosphate buffer:tert-butyl alcohol solution, pH 8.1, at 0.10 $V.s^{-1}$, glassy carbon working electrode.

The UV-vis spectra in CH_2Cl_2 and in aqueous solution at pH 8.1 are shown in Figures 7 and 8, respectively. The bands at λ=484 nm and 480 nm can be attributed to metal-to-ligand $d\pi(Ru) \rightarrow \pi^*$ (diphosphine) transitions and the bands at λ=448 nm and 444 nm can be attributed to metal-to-ligand $d\pi(Ru) \rightarrow \pi^*$ (polypyridyl) transitions (Sussuchi, Lima, & De Giovani, 2006). According to the literature (Wu et al., 2017; Khade, Choudhury, & Pal, 2018), cyclic voltammograms of ruthenium (II) aqua complexes, such as those studied here, exhibit two reversible redox waves involving concomitant transfers of protons and electrons: $[Ru^{II}(L)(totpy)OH_2]^{2+}/[Ru^{III}(L)(totpy)OH]^{2+}/[Ru^{IV}(L)\ (totpy)O]^{2+}$ (corresponding to the $Ru^{IV/III}$ and $Ru^{III/II}$ couples, as observed in cyclic voltammogram in aqueous medium, pH 8.1 (Figure 10, Table 2). On the other hand, the cyclic voltammogram in CH_2Cl_2 shows three pairs of redox waves (Figure 9, Table 2). The EPR spectrum of the aqua complex in CH_2Cl_2 has indicated small percentage of Ru (III), which may explain the three redox pairs observed in the voltammogram. However, monitoring the aqua complex in CH_2Cl_2, by differential pulse voltammetry (DPV), one could observe the disappearing of the redox pair at +0.72 V, possibly indicating an isomeric interconversion process, whereby the small part of terpyridyl diphosphine aqua complex in oxidation state (III) is reduced to state (II) when in solution.

Attempt to purify the aqua complex $[Ru(L)(totpy)(OH_2)](ClO_4)_2$ using a neutral Al_2O_3 column (58 Å, ~150 mesh) with CH_2Cl_2 as eluent was not successfull. The use of an SP-Sephadex C-25 cation exchange column (Marmion & Takeuchi, 1988), eluting with 0.20 mol L^{-1} $NaClO_4$ solution, has caused decomposition of the complex. Using a Merck silica gel column (40 Å, 35-70 mesh), eluting with different chloroform:methanol ratios, complex decomposition has not occurred. However, no change has been observed in the cyclic and DPV voltammograms, and in UV-vis and EPR spectra.

It is worth to note that a similar aqua complex, containing $Ph_2AsCH_2CH_2AsPh_2$ ligand presents cyclic voltammetric, UV-vis spectrum and elemental analysis data in agreement with the aqua complex synthesized in this work (Batalini & De Giovani, 2019). In prolonged tests of differential pulse voltammetry this kind of complexes has demonstrated high stability, without loss of ligands, as verified in the studies carried out by Meyer (1984), Tse et al. (2005) and Ezhilarasu et al. (2017). We have used ruthenium aquacomplexes containing substituted terpyridine and bidentate ligands as catalysts in electrooxidations of alcohols in homogeneous solution (Batalini & De Giovani, 2020); the electrocatalysis have shown selective reactions with good yields, whose process is in progress aligned with several Green Chemistry criteria.

Conclusion

The aim of this work was to synthesize a ruthenium aqua complex with the unprecedented combination of a substituted terpyridine ligand and a bidentate phosphine ligand. The proposed three-step synthesis strategy to obtain the diphosphine aqua complex $[Ru(L)(totpy)(OH_2)](ClO_4)_2$ *(L=*$Ph_2PCH_2CH_2PPh_2$*) (totpy=4´-(4-tolyl)-2,2´:6´,2´´-terpyridine)* was successfully achieved. Very good reaction yields have been obtained for each one of the reaction steps (1st step 78%, 2nd step 85%, 3rd step 66%). Elemental analysis, cyclic voltammetric and UV-vis spectroscopic data support the proposed chemical structure for the aqua complex.

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References

Abid, M., Shamsi, F., & Azam, A. (2016). Ruthenium complexes: an emerging ground to the development of metallopharmaceuticals for cancer therapy. *Mini-Reviews in Medicinal Chemistry*, *16*(10), 772-786. DOI: https://doi.org/10.2174/1389557515666151001142012

Almeida, M. A. P., Nascimento, F. B., Graminha, A. E., Ferreira, A. G., Ellena, J., Mello, F. M. S., ... Batista, A. A. (2014). Structural features and cytotoxic activities of $[Ru(AA\text{-}H)(dppb)(bipy)]PF_6$ complexes, *Polyhedron*, *81*, 735-742. DOI: https://doi.org/10.1016/j.poly.2014.07.024

Ameta, S. C., & Ameta, R. (2016). *Solar energy conversion and storage*. CRC Press: Boca Raton, USA.

Basset, J. (1981). *Vogel - Análise Inorgânica Quantitativa* (4a. ed.). Rio de Janeiro, RJ: Editora Guanabara.

Batalini, C., & De Giovani, W. F. (2019). Síntese e caracterização de um novo aquacomplexo diarsínico de Rutênio (II). *Periódico Tchê Química*, *16*(32), 130-138. DOI: https://doi.org/10.52571/PTQ.v16.n32.2019.148_Periodico32_pgs_130_138.pdf

Batalini, C., & De Giovani, W. F. (2020). Electrochemical oxidations of organic substances using a new ruthenium (II) diarsenic aquacomplex as catalyst. *Periódico Tchê Química, 17*(34), 62-66. DOI: https://doi.org/10.52571/PTQ.v17.n34.2020.80_P34_pgs_62_66.pdf

Chaudret, B., Delavaux, B., & Poilblanc, R. (1988). Bisdiphenylphosphinomethane in dinuclear complexes. *Coordination Chemistry Reviews*, *86*, 191-243. DOI: https://doi.org/10.1016/0010-8545(88)85014-8

Constable, E. C., Ward, M. D., & Corr, S. (1988). A convenient, high yield synthesis of 2,2′:6′,2″-terpyridine and its iron (II) complex. *Inorganica Chimica Acta*, *141*(2), 201-203. DOI: https://doi.org/10.1016/S0020-1693(00)83910-9

Cristian, L., Nica, S., Pavel, O. D., Mihailciuc, C., Almasan, V., Coman, S. M., ... Parvulescu, V. I. (2013). Novel ruthenium-terpyridyl complex for direct oxidation of amines to nitriles. *Catalysis Science & Technology*, *3*(10), 2646-2653. DOI: https://doi.org/10.1039/c3cy00209h

Delgado, J., Zhang, Y., Xu, B., & Epstein, I. R. (2011). Terpyridine- and bipyridine-based ruthenium complexes as catalysts for the Belousov-Zhabotinsky reaction. *The Journal of Physical Chemistry A*, *115*(11), 2208-2215. DOI: https://doi.org/10.1021/jp111724t

Dovletoglou, A., Adeyemi, S. A., & Meyer, T. J. (1996). Coordination and redox chemistry of substituted-polypyridyl complexes of ruthenium. *Inorganic Chemistry*, *35*(14), 4120-4127. DOI: https://doi.org/10.1021/ic9512587

Ezhilarasu, T., Sathiyaseelan, A., Kalaichelvan, P. T., & Balasubramanian, S. (2017). Synthesis of 4′-substituted-2, 2′; 6′, 2″-terpyridine Ru (II) complexes electrochemical, fluorescence quenching and antibacterial studies. *Journal of Molecular Structure*, *1134*, 265-277. DOI: https://doi.org/10.1016/j.molstruc.2016.12.102

Gao, J. X., Wan, H. L., Wong, W. K., Tse, M. C., & Wong, W. T. (1996). Synthesis and characterization of iron (2+) and ruthenium (2+) diimino-, diamino- and diamido-diphosphine complexes. X-ray crystal structure of trans-$RuCl_2(P_2N_2C_2H_4)$ ∗d $CHCl_3$. *Polyhedron*, *15*(8), 1241-1251. DOI: https://doi.org/10.1016/0277-5387(95)00385-1

Gericke, R., & Wagler, J. (2017). Phosphorus as Lone Pair Donor and Ligand Acceptor: A Paddlewheel with Ru←P Axis. *European Journal of Inorganic Chemistry*, *2018*(1), 86-90. DOI: https://doi.org/10.1002/ejic.201701386

Hanabusa, K., Nakamura, A., Koyama, T., & Shirai, H. (1994). Electropolymerization and characterization of terpyridinyl iron (II) and ruthenium (II) complexes. *Polymer International*, *35*(3), 231-238. DOI: https://doi.org/10.1002/pi.1994.210350303

Khade, R. V., Choudhury, S. D., Pal, H., & Kumbhar, A. S. (2018). Excited state interaction of ruthenium (II) imidazole phenanthroline complex $[Ru(bpy)_2ipH]^{2+}$ with 1,4-benzoquinone: Simple electron transfer or proton-coupled electron transfer? *ChemPhysChem*, *19*(18), 2380-2388. DOI: https://doi.org/10.1002/cphc.201800313

Lima, E. C., Fenga, P. G., Romero, J. R., & De Giovani, W. F. (1998). Electrochemical behaviour of $[Ru(4,4'\text{-}Me_2bpy)_2(PPh_3)(H_2O)](ClO_4)_2$ in homogeneous solution and incorporated into a carbon paste electrode. Application to oxidations of benzylic compounds. *Polyhedron*, *17*(2), 313-318. DOI: https://doi.org/10.1016/S0277-5387(97)00306-9

Lin, K., Zhao, Z.-Z., Bo, H.-B., Hao, X.-J., & Wang, J.-Q. (2018). Applications of ruthenium complex in tumor diagnosis and therapy. *Frontiers in Pharmacology*, *9*. DOI: https://doi.org/10.3389/fphar.2018.01323

Malecki, J. G. (2012). Half-sandwich ruthenium (II) complexes with N and N,(N,O) donor ligands: molecular, electronic structures, and computational study. *Structural Chemistry, 23*, 461-472. DOI: https://doi.org/10.1007/s11224-011-9890-0

Marmion, M. E., & Takeuchi, K. J. (1988). Ruthenium (IV)-oxo complexes: the novel utilization of tertiary pnicogen ligands. *Journal of the American Chemical Society*, *110*(5), 1472-1480. DOI: https://doi.org/10.1021/ja00213a019

Mello-Andrade, F., Cardoso, C. G., Silva, C. R. E., Chen-Chen, L., Melo-Reis, P. R., Lima, A. P., ... Silveira-Lacerda, E. P. (2018). Acute toxic effects of ruthenium (II)/amino acid/diphosphine complexes on Swiss mice and zebrafish embryos. *Biomedicine & pharmacotherapy, 107*, 1082–1092. DOI: https://doi.org/10.1016/j.biopha.2018.08.051

Meyer, T. J. (1984). Redox pathways: applications in catalysis. *Journal of the Electrochemical Society*, *131*(7), 221-C. Retrieved from https://iopscience.iop.org/article/10.1149/1.2115949/pdf

Morita, T., & Assumpção, R. M. V. (2007). *Manual de soluções, reagentes e solventes* (2a. ed.). São Paulo, SP: Ed. Blucher.

Sadig, A., & Nazeeruddin, M. K. (2018). Ruthenium complexes as sensitizers in dye-sensitized solar cells. *Inorganics*, *6*(2), 52-86. DOI: https://doi.org/10.3390/inorganics6020052

Sawyer, D. T., & Roberts, J. L. (1974). *Experimental Electrochemistry for Chemists*. New York, US: John Wiley & Sons.

Spahni, W., & Calzagerri, G. (1984). Synthese von *para*-substituierten phenyl-terpyridin liganden. *Helvetica Chimica Acta*, *67*(2), 450-454. DOI: https://doi.org/10.1002/hlca.19840670214

Sullivan, B. P., Calvert, J. M., & Meyer, T. J. (1980). Cis-trans isomerism in $(trpy)(PPh_3)RuCl_2$. Comparisons between the chemical and physical properties of a cis-trans isomeric pair. *Inorganic Chemistry*, *19*(5), 1404-1407. DOI: https://doi.org/10.1021/ic50207a066

Sullivan, B. P., Salmon, D. J., & Meyer, T. J. (1978). Mixed phosphine 2,2'-bipyridine complexes of ruthenium. *Inorganic Chemistry*, *17*(12), 3334-3341. DOI: https://doi.org/10.1021/ic50190a006

Sussuchi, E. M., Lima, A. A., & De Giovani, W. F. (2006). Effect of the cis- and trans-[1,2-bis(diphenylphosphino)ethylene] ligands in the properties of diphosphine–polypyridyl complexes of ruthenium(II): Application to electrocatalytic oxidations of organic compounds. *Journal of Molecular Catalysis A: Chemical*, *259*(1), 302-308. DOI: https://doi.org/10.1016/j.molcata.2006.05.059

Sussuchi, E. M., Lima, A, A., & De Giovani, W. F. (2006). Synthesis and eletrochemical, spectral and catalytic properties of diphosphine-polypyridil ruthenium complexes. *Polyhedron, 25*(6), 1457-1463. DOI: https://doi.org/10.1016/j.poly.2005.10.009

Thota, S., Rodrigues, D. A., Crans, D. C., & Barreiro, E. J. (2018). Ru (II) compounds: next-generation anticancer metallotherapeutics? *Journal of Medicinal Chemistry*, *61*(14), 5805-5821. DOI: https://doi.org/10.1021/acs.jmedchem.7b01689

Tse, M. K., Klawonn, M., Bhor, S., Döbler, C., Anilkumar, G., Hugl, H., ... Beller, M. (2005). Convenient method for epoxidation of alkenes using aqueous hydrogen peroxide. *Organic Letters*, *7*(6), 987-990. DOI: https://doi.org/10.1021/ol047604i

Van Ravensteijn, B. G. P., Schild, D. -J., Kegel, W. K., & Klein Gebbink, R. J. M. (2017). The immobilization of a transfer hydrogenation catalyst on colloidal particles. *ChemCatChem - Catalysis*, *9*(3), 440-450. DOI: https://doi.org/10.1002/cctc.201601096

Wang, J.-Q., Zhang, P.-Y., Qian, C., Hou, X.-J., Ji, L.-N., & Chao, H. (2014). Mitochondria are the primary target in the induction of apoptosis by chiral ruthenium(II) polypyridyl complexes in cancer cells. *Journal of Biological Inorganic Chemistry, 19*(3), 335-348. DOI: https://doi.org/10.1007/s00775-013-1069-2

Wu, S.-H., Shao, J.-Y., Dai, X., Cui, X., Su, H., & Zhong, T.-W. (2017). Synthesis and characterization of tris(bidentate) ruthenium complexes of di(pyrid-2-yl)(methyl)amine. *European Journal of Inorganic Chemistry, 2017*(24), 3064-3071. DOI: https://doi.org/10.1002/ejic.201700291

Zeng, L., Gupta, P., Chen, Y. Wang, E., Ji, L., Chao, H., & Chen, Z. S. (2017). The development of anticancer ruthenium(II) complexes: from single molecule compounds to nanomaterials. *Chemical Society Review*, *46*(19), 5771-5804. DOI: https://doi.org/10.1039/c7cs00195a