

Electrochemical evaluation of two polyaza Ru(II) complexes as sensitizing materials in photocatalysis

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ABSTRACT

This paper reports the synthesis and electrochemical characterization of two new polyaza complexes of Ruthenium(II). These complexes were obtained from the direct reaction between RuCl_3 and the N^1 -(2-aminebenciliden)- N^2 , N^2 -bis(2-(2-aminebenciliden)amine)ethyl)ethane-1,2-diamine (L1), and N^1, N^2 -bis(2-aminebenciliden)ethane-1,2-diamine (L2) polyaza-type ligands. The complexes were characterized by infrared (IR) spectroscopy, by their fusion point, and by elementary analysis (EA) and fluorescence analysis (FA), to determine their chemical properties. The redox potentials of Ru(II) [Ru(II)/Ru(III) and Ru(III)/Ru(II)] were determined for each synthesized complex using the cyclic voltammetry (CV) technique. The electrochemical characterization was performed with an Au electrode modified by chemisorption with each complex after depositing a mercaptopropionic acid (MPA) layer. The obtained redox potential values show that the complexes can inject electronic charge into the conduction band (CB) of the TiO_2 semiconductor, which enhances its photocatalytic activity under visible light and allows the application of this sensitized material in photocatalytic processes with higher efficiency and sustainability.

KEYWORDS: complexes, polyaza, cyclic voltammetry, TiO_2 , modified electrodes, ruthenium.

1. INTRODUCTION

Several studies report that the complexes derived from polidentate ligands with stable structures and high conjugation have been used to modify the surface of semiconductor oxides because of their capacity to absorb visible light [1-7].

Among these complexes, Ru(II) complexes have fluorescent properties; hence, when these complexes are incorporated to the surface of a photocatalytic semiconductor such as TiO_2 , they can inject electronic charge from their excited state to the oxide CB, which makes their activation possible in the visible light region [8-14]. Determining the redox potentials of these complexes with respect to the redox potentials of the CB and the valence band (VB) of the semiconductor is very important to evaluate the capacity of the complexes to inject charge into the semiconductor [15-18].

In this work we synthesized two Ru(II) complexes derived from polyaza-type ligands N^1 -(2-aminebenciliden)- N^2, N^2 -bis(2-(2-aminebenciliden)amine)ethyl)ethane-1,2-diamine (L1) and N^1, N^2 -bis(2-aminebenciliden)ethane-1,2-diamine (L2). We characterized the obtained complexes by IR spectroscopy, by their fusion point, and by EA and FA. We also studied the electrochemical behavior using the CV technique to determine the redox potentials and evaluate their possible application as photocatalytic material sensitizers [4, 19-21].

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2. MATERIALS AND METHODS

2.1. Synthesis of RuL1 and RuL2 complexes

2.1.1. Synthesis of L1 and L2 ligands

L1 and L2 ligands were obtained using the Schiff base condensation reaction between 2-aminebenzaldehyde and tris(2-amineethyl)amine and ethylenediamine, respectively (Figure 1). This reaction was carried out in a methanolic medium with constant sonochemical agitation using an ultrasonic dismembrator. The 2-aminebenzaldehyde precursor was previously obtained by reduction of 2-nitrobenzaldehyde in an HCl medium in the presence of Fe^0 .

2.1.2. Synthesis of RuL1 and RuL2 complexes

These complexes were synthesized by direct reaction between a saturated dissolution of each ligand and

another dissolution of Ru(III) salt in an ethylene glycol medium (Figure 2). This reaction was carried out under sonochemical agitation using an ultrasonic dismembrator. The obtained complexes were characterized by IR spectroscopy, fusion point, EA, and by FA.

2.2. Electrochemical characterization of the complexes

2.2.1. Au electrode modification

We used a traditional three-electrode electrochemical cell with 50 mL capacity. We used an Au surface as the working electrode, a Pt wire as the auxiliary electrode, and Ag/AgCl (3 molL^{-1} KCl) as the reference electrode. We prepared the dissolutions using analytic reactive-grade chemical products and deionized water.

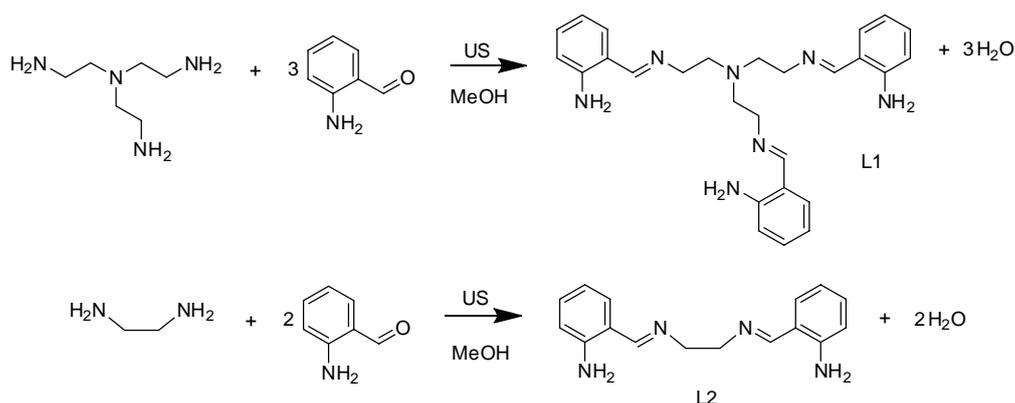


Figure 1. Synthesis of L1 and L2 ligands.

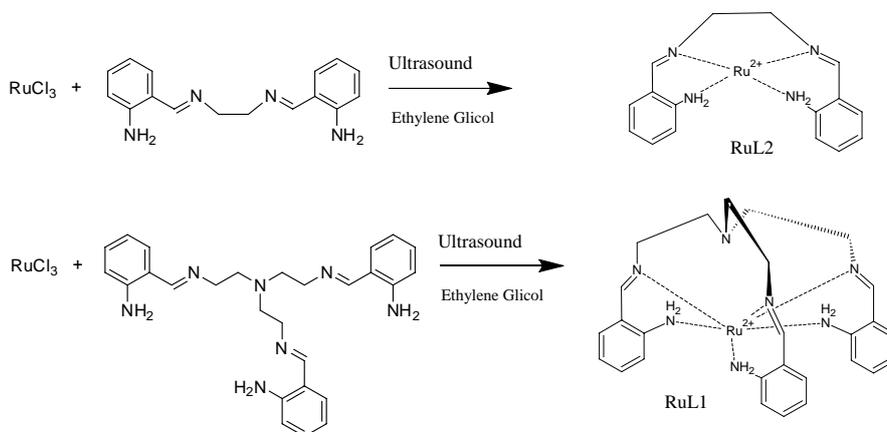


Figure 2. Synthesis of the RuL1 and RuL2 complexes.

Before modifying the Au electrode surface, we applied for one minute a potential of -1.0 V vs the Ag/AgCl electrode potential to the system in an aqueous deoxygenated H_2SO_4 0.5 molL^{-1} solution. The electrode cleaning was performed this way to ensure an adequate surface area for modification with MPA. We modified the Au electrode following a two-step sequence. In the first step, we introduced the clean electrodes in MeOH with 1 mmolL^{-1} of MPA for 24 hours to generate a surface functionalized with carboxylate groups. In the second step, we washed the functionalized electrodes with dimethylformamide (DMF) and placed them in a 1 mmolL^{-1} dissolution of each Ru(II) complex for 24 hours. Under these conditions, the counter ion of the metallic complexes moves through the carboxylate groups immobilized on the Au electrode surface, in such a way that the formed ion pair provides the fixation on the electrode of the complexes of interest.

2.2.2. Determination of the redox potentials of the ligands and their complexes

The redox potentials of the ligands and the Ru(II) complexes were determined by CV. We used a BAS potentiostat, which was connected to an electrochemical cell with a 0.1 molL^{-1} NaNO_3 dissolution as the electrolytic medium, a Pt wire as the counter electrode, and an Ag wire as the pseudo-reference electrode [2]. We used the Au electrodes modified as described in Subsection 2.2.1 as the working electrodes. All the potentials were later recalculated with reference to the NHE [22].

3. RESULTS AND DISCUSSION

Table 1 shows the main chemical and spectroscopic properties of the ligands and their complexes. The fact that the fusion points of the ligands are lower

than those of their complexes indicate that the complexes have higher thermal stability. The spectra obtained by FA show an emission in the visible region for the complexes. The IR spectra show absorption bands of the ligands in the complexes, but with a shift of the signals to lower wavelengths, which suggests an interaction between Ru(II) and the ligand heteroatomic groups. These differences in their properties and the coherency of the EA results for the proposed structures indicate the obtention of Ru(II) complexes.

Figure 3 depicts the voltammogram obtained for the H_2 evolution in the presence of H_2SO_4 1 molL^{-1} . The voltammogram shows the oxidation processes on the surface of the golden electrode in the presence of H^+ when a surface cleaning is applied [23].

Figure 4 shows the CV for the electrode modification with the MPA monolayer in the presence of N_2 , with a 0.01 molL^{-1} concentration. The curve shows the acid desorption peak at -1.3 V vs Ag/AgCl, which results from the reduction of the functional groups of the thiol molecule [22].

Figure 5 shows the voltammograms of the ligands and their Ru(II) complexes. The peaks present in the RuL1 complex around 0.5 V vs Ag/AgCl indicate that the transfer current is controlled by the electron flow in the metal (the N-Ru interactions present in the complex) and the reduction of the imine groups present in the ligand molecule. These peaks with similar potential (0.55 V and 0.60 V vs Ag/AgCl) suggest the possibility of a reactivity increase of the functional groups present in the ligand. However, the presence of only one oxidation peak suggests that an heteroatom involved in the coordination sphere has an irreversible transformation.

Table 1. Comparison of the chemical and spectroscopic properties of the synthesized complexes.

Compound	F.P. °C	λ Emission nm	IR Signals cm^{-1} N-H; C-N; C=N	EA C - N - H Exp % (Theor %)
L1	117	340	3400; 1230; 1560	71.0(71.2); 6.9(7.3); 21.1(21.5)
RuL1	241	530	3330; 1120; 1510	47.1(47.6); 4.3(4.9); 18.0(18.5)
L2	125	385	3470; 1270; 1550	72.8(72.2); 7.0(6.8); 20.4(21.0)
RuL2	264	445; 560	3310; 1050; 1500	38.8(39.1); 3.5(3.7); 16.7(17.1)

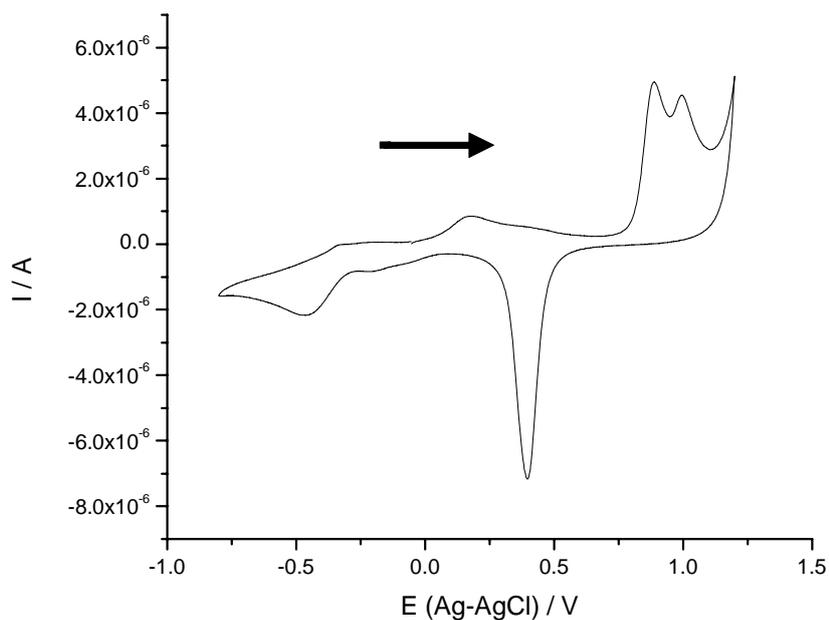


Figure 3. Voltammogram for the Au electrode in H_2SO_4 1 molL^{-1} . v : 50 mVs^{-1} .

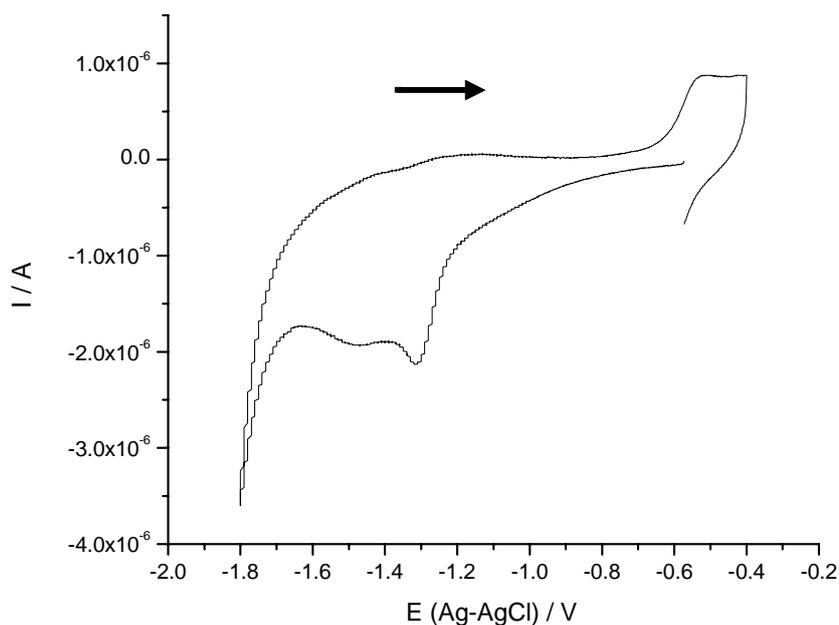


Figure 4. Cyclic voltammetry of Au (0.01 molL^{-1} of MPA)/ NaNO_3 0.01 molL^{-1} . v : 100 mVs^{-1} .

This current transfer phenomenon could not be observed in the case of the L2/RuL2 system, probably because the conditions were not ideal for this system as the apparent oxidation peak is masked by the oxidation process in the solvent. The appearance of the peaks in the complex

voltammograms and their potentials indicate the coordination of the heteroatoms with the metal, and also suggests that the metal present in the coordination sphere of the complexes favors the current diffusion and contributes to their stability in a wide range of applied potentials [24, 25].

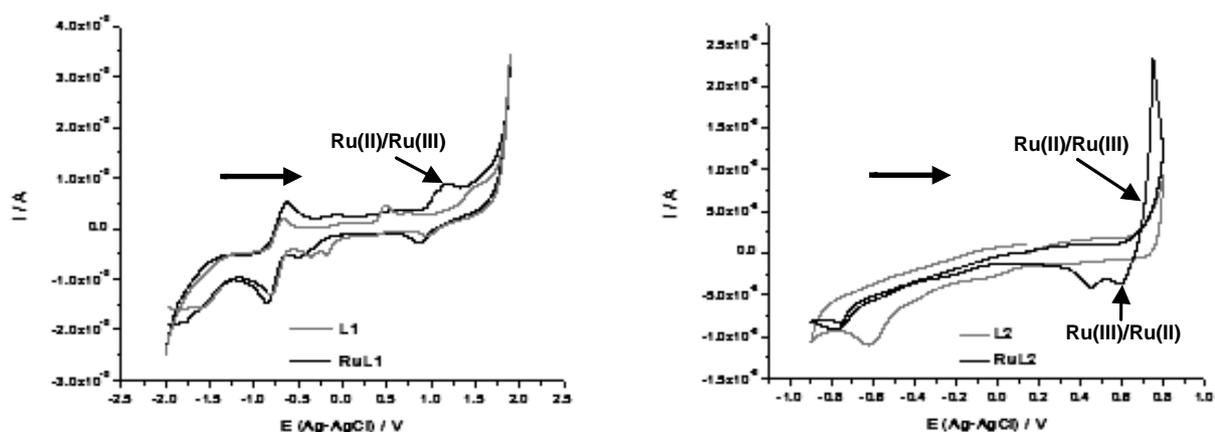


Figure 5. Voltammograms of the ligands and complexes incorporated in Au(0.01 molL⁻¹ of MPA)/NaNO₃ 0.01 molL⁻¹. v: 50 mVs⁻¹.

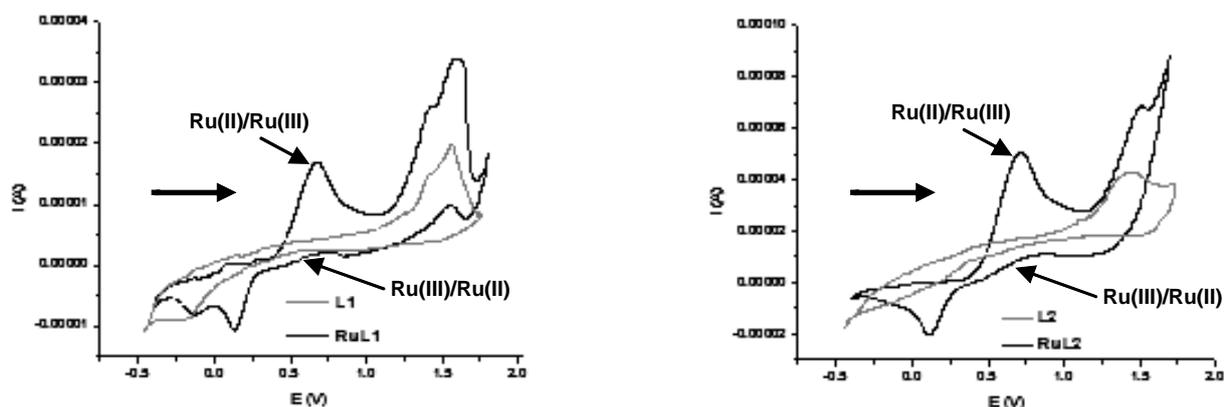


Figure 6. Voltammograms of the ligands and complexes incorporated in Au(0.01 molL⁻¹ of MPA)/BF₆(Bu)₄NH₄ 0.01 molL⁻¹. v: 50 mVs⁻¹.

Table 2. Redox potential values for the studied systems (E vs NHE).

System	E _R , V	E _{OX} , V
Au RuL1	-2.55 [Ru(III) Ru(II)]	+0.15 [Ru(II) Ru(III)]
Au L1	-1.00	+0.05
Au RuL2	-2.40 [Ru(III) Ru(II)]	+0.35 [Ru(II) Ru(III)]
Au L2	-1.4	+0.25

Figure 6 shows that in a organic solvent (ACN) the peaks are more clearly resolved while running the same voltammetric process, as the ligands and complexes are closely incorporated to the Au electrode allowing a better resolution for the redox processes of Ru. Table 2 summarizes the obtained

redox potentials of both complexes (E vs NHE). The table shows that the reduction potentials of the complexes are more negative than the potential corresponding to the TiO₂ CB. This reduction potential change due to the formation of both complexes favors the charge injection into the TiO₂ CB.

For evaluating the application of these substances as possible semiconductor surface sensitizers it is important to determine their redox potential values. For both complexes, the reduction potential was more negative (-2.55 V vs NHE) than that of the TiO₂ CB (-0.52 V vs NHE, the potential for which electrons migrate from the VB to the CB of TiO₂), which is adequate for an effective electron injection to TiO₂. These potential conditions might enhance the TiO₂ activity under visible light [14, 26].

4. CONCLUSIONS

We performed the synthesis and the electrochemical characterization of two new polyaza complexes of Ru(II). We modified Au electrodes with the ligands and complexes obtained on an MPA monolayer previously deposited on the Au surface. The MPA voltammogram indicate the presence of this monolayer, which allowed modifying the Au electrode with the ligands and their complexes with Ru(II). The results of the polyaza RuL1 complex CV study suggest that it has electronic charge transfer properties because the reduction potentials of the obtained complexes are more negative than the redox potentials of the TiO₂ and VB. This result indicates that the complexes can inject electronic charge to the TiO₂ CB, thus sensitizing the semiconductor, which enhances its photocatalytic activity.

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CONFLICT OF INTEREST STATEMENT

The authors hereby declare that there is no conflict of interest.

REFERENCES

- Lee, C., Zhang, Y., Romayanantakit, A. and Galoppini, E. 2010, *Tetrahedron*, 66, 3897-3903.
- Góngora, J., Elizondo, P., Pérez, N., Villanueva, M., Hinojosa, L. and Hernández, A. 2014, *Ceram. Int.*, 40, 14207-14214.
- Onozawa, N., Yanagida, M., Funaki, T., Kasuga, K., Sayama, K. and Sugihara, H. 2009, *Inorg. Chem. Commun.*, 12, 1212-1215.
- Kar, P., Verma, S., Sen, A., Das, A., Ganguly, B. and Ghosh, H. 2010, *Inorg. Chem.*, 49, 4167-4174.
- Banerjee, S. and Pillai, S. 2014, *J. Phys. Chem. Letters*, 5, 2543-2554.
- Boreen, A., Arnold, W. and McNeill, K. 2003, *Aquat. Sci.*, 65, 320-341.
- Fan, S., Kim, C., Fang, B. and Liao, K. 2011, *J. Phys. Chem. C*, 7747-7754.
- Boyer, S., Liu, J. and Zhang, S. 2016, *J. Photochem. Photobiol. A Chem.*, 329, 46-53.
- Funaki, T., Yanagida, M., Onozawa, N., Kawanishi, Y., Kasuga, K. and Sugihara, H. 2009, *Sol. Energy Mater. Sol. Cells*, 93, 729-732.
- De Angelis, F. and Vitillaro, G. 2012, *J. Phys. Chem. C*, 1, 18124-18131.
- Vougioukalakis, G., Philippopoulos, A., Stergiopoulos, T. and Falaras, P. 2011, *Coord. Chem. Rev.*, 255, 2602-2621.
- Góngora, J., Elizondo, P. and Hernandez, A. 2016, *Photochem. Photobiol. Sci.*, 16, 31-37.
- Bin, B., Peng, Y., Tao, T., Geng, J. and Huang, W. 2015, *Dye. Pigment.*, 117, 100-107.
- Brown, D., Schauer, P., Borau, J., Fancy, B. and Berlinguette, C. 2013, *J. Am. Chem. Soc.*, 135, 1692-1695.
- Henderson, M. 2011, *Surf. Sci. Rep.*, 66, 185-297.
- Emeline, A., Kuznetsov, V., Rybchuk, V. and Serpone, N. 2008, *Int. J. Photoenergy*, 27, 1-19.
- Belver, C., Bellod, R., Stewart, S., Requejo, F. and Fernández, M. 2006, *Appl. Catal. Environ.*, 65, 309-314.
- Sakkas, V., Islam, M., Stalikas, C. and Albanis, T. 2010, *J. Hazard. Mater.*, 175, 33-44.
- Lee, J. and Yang, M. 2011, *Mater. Sci. Eng. B*, 176, 1142-1160.
- Armelaio, L. and Quici, S. 2010, *Coord. Chem. Rev.*, 254, 487-505.
- Park, H., Park, Y., Kim, W. and Choi, W. 2013, *J. Photochem. Photobiol. C Photochem. Rev.*, 15, 1-20.
- Liu, S., Li, X., Li, Y., Li, Y., Li, J. and Jiang, L. 2005, *Electrochim. Acta*, 51, 427-431.

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23. Coustan, L., Shul, G. and Bélanger, D. 2017, *Electrochem. Commun.*, 14, 785-793.
 24. Mohamed, R., Elantabli, F., Helal, N. and Medani, S. 2015, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, 141, 316-326.
 25. La, M., Feng, Y., Yang, C. and Chen, C. 2014, *Int. J. Electrochem. Sci.*, 9, 6985-6992.
 26. Malato, S., Fernández, P., Maldonado, M., Blanco, J. and Gernjak, W. 2009, *Catal. Today*, 147, 1-59.