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**Efeitos Sinérgicos em Complexos Binucleares de
Rutênio com um Ligante Benzobisimidazol em
Ponte, Precursores de Catalizadores para Oxidação
da Água**

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**Synergistic Effect in Ruthenium Complexes Bridged
by a Benzobisimidazole Ligand, Precursors of Water
Oxidation Catalysts**

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*A mi madre y mi abuela por ser mi mejor ejemplo,
esas raíces fuertes que motivan mi crecimiento.
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RESUMO

Benavides, P. A. **Efeitos Sinérgicos em Complexos Binucleares de Rutênio com um Ligante Benzobisimidazol em Ponte, Precursores de Catalizadores para Oxidação da Água**. 2017. 93p. Dissertação de Mestrado Programa de Pós-Graduação em Química. Instituto de Química, Universidade de São Paulo, São Paulo.

Este trabalho está focado no desenvolvimento de complexos de rutênio binucleares baseados no ligante ponte 2,6-bis(2-piridil)benzodiimidazol (dpimH_2) com potencial aplicação como catalisadores para oxidação da água. O acoplamento eletrônico entre os centros metálicos bem como as propriedades eletrônicas e catalíticas podem ser controlados via reações ácido-base no ligante bis-bidentado. Dessa forma, neste trabalho descrevemos o preparo e a caracterização do respectivo composto mononuclear, bem como do complexo binuclear simétrico $[\{\text{RuCl}(\text{phtpy})\}_2(\text{dpimH}_2)](\text{Otf})_2$ (onde phtpy =4-fenil-2,2':6',2''-terpiridina), e do análogo assimétrico $[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}](\text{ClO}_4)_3$ (onde bpy =2,2'-bipyridina), que possui um centro catalítico e um grupo cromóforo na mesma molécula como esperado em um fotocatalisador, em que os dois centros catalíticos estão covalentemente conectados através do ligante ponte funcional. As caracterizações estrutural e eletrônica de ambos os complexos por ^1H RMN, ESI-MS e espectroscopia de absorção UV-Vis indicaram a presença de isômeros geométricos com perfis eletrônicos similares. Por outro lado, a análise eletroquímica por voltametria cíclica demonstrou menores potenciais Ru(III/II) quando comparados a complexos polipiridínicos análogos. Este potencial redox pode ainda ser catodicamente deslocado através da remoção de prótons dos grupos imidazóis do ligante ponte, possibilitando, dessa forma, a modulação das propriedades eletrônicas e catalíticas destes complexos de rutênio através de reações de protonação/desprotonação dos grupos $-\text{NH}$. Além disso, neste trabalho é investigada a inesperada formação do complexo $[\text{Ru}(\text{phtpy})_2]$ nas reações do complexo $[\text{RuCl}_3(\text{phtpy})]$ puro com ligantes bidentados, utilizando-se espectroscopia UV-Vis e de ^1H RMN.

Palavras-Chave: Catalisador, Oxidação de Água, Complexos Binucleares, Eletroquímica, Díade Cromóforo-Catalisador, Ligante Ponte Funcional.

ABSTRACT

Benavides, P. A. **Synergistic Effect in Ruthenium Complexes Bridged by a Benzobisimidazole Ligand, Precursors of Water Oxidation Catalysts.** 2017. 93p. Master Thesis - Graduate Program in Chemistry. Instituto de Química, Universidade de São Paulo, São Paulo.

This work is focused on the development of dinuclear ruthenium complexes with potential application as catalysts for oxidation of water, that are characterized by a benzobisimidazole 2,6-bis(2-pyridyl)benzodiimidazole (dpimH₂) bridging ligand, whose interaction between the metal centers as well as the electronic and catalytic properties can be tuned by acid-base reactions in that moiety. Thus, the preparation and characterization of the respective mononuclear species are described. The dinuclear complex $[\{\text{RuCl}(\text{phtpy})\}_2(\text{dpimH}_2)](\text{Otf})_2$ (phtpy=4-phenyl-2,2':6',2''-terpyridine), in which two catalytic centers are covalently linked through that bridging ligand, and of the $[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}](\text{ClO}_4)_3$ complex (where bpy=2,2'-bipyridine) integrating a chromophore and a catalytic center in the same molecule as expected for a photocatalyst. The structural and electronic characterization of both complexes by NMR, ESI-MS and UV-vis spectroscopy indicated the presence of geometric isomers with similar electronic profiles. On the other hand, the electrochemical analysis by cyclic voltammetry displayed redox potential values for the Ru³⁺/Ru²⁺ couples lower than the respective polypyridyl complex counterparts. This redox potential can be even more shifted to less positive potentials by removal of protons from the imidazole groups in the bridging ligand, opening the possibility of tuning the electronic and catalytic properties of those ruthenium complexes based on protonation/deprotonation of the -NH groups. Furthermore, in this work is analyzed the unexpected formation of the bisterpyridine $[\text{Ru}(\text{phpy})_2]$ complex in reactions starting with pure $[\text{RuCl}_3(\text{phtpy})]$ complex with bidentated ligands, as through UV-Vis spectroscopy and RMN.

Keywords: Water oxidation catalyst, Dinuclear Complexes, Benzobisimidazole, Chromophore-Catalyst Dyad, Electronic Coupling

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LIST OF ABBREVIATIONS

IEA	International Energy Agency
Mtoe	Million tonnes of oil equivalent
TW	Terawatts
GHGs	Greenhouse gas emissions
PCET	Proton coupled electron transfer
CAN	Cerium ammonium nitrate
TOF	Turn over frequency
TON	Turn over number
I2M	Interaction between two M–O entities
WNA	Water nucleophilic attack
NEM	N-ethylmorpholine
TEA	Triethylamine
CV	Cyclic Voltammogram
DPV	Differential Pulse Voltammetry

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I. Introduction

The growth of world population and the rise of developed and emerging economies bring with them an increasing demand for energy that is mostly supplied by fossil fuel resources. According to the International Energy Agency (IEA),¹ until 2013, eighty-one percent of the total global energy supply came from fossil fuels, including coal/peat, petroleum, and natural gas (figure 1).

Figure 1. World total primary energy supply from 1971 to 2013 by fuel (Mtoe). In these graphs; 2. Peat and shale oil are aggregated with coal and 3. Includes geothermal, solar, wind, heat, etc. (Taken from ref. 1)

As a result of a codependent relationship between economic development and the use of fossil fuels, the emission levels of carbon dioxide have increased up to 6.6 metric tons of coal per year, with relatively steady increase, reaching the highest values recorded in the last 800.000 years. Additionally, the burning and consumption of fossil fuels entail the generation of other harmful greenhouse gases such as: carbon monoxide, methane, nitrous oxides and other volatile gases, not to mention the damage to ecosystems caused by exploration of these energy resources.^{2,3}

Currently, the global energy demand is 13 TW and is expected that in 2050, given the dynamics of consumption and the global economic growth, this value will rise to 50 TW.⁴ This is an alarming number, bearing in mind that the current greenhouse gas emissions (GHGs) are generating a climate change responsible for various weather-related calamities such as drought, heat waves, floodings and hurricanes.⁵ Given this grim picture, one of the current challenges facing humanity is the development of alternative carbon-free energy sources that allow maintaining the emission of carbon dioxide and other volatile gases under acceptable levels.

Since alternative energy sources such as hydroelectric and nuclear plants have an environmental and social cost that limits its use as a definitive solution to obtain carbon-free fuel resources, energy from the sun has been raised as the most promising and attractive alternative, as it is clean and sustainable energy source.

Today, a variety of photovoltaic devices capable of converting sunlight into electricity, are very common to be found. However, it is also notable that the operation of these devices is limited by the intermittent and diffuse nature of sunlight, making necessary the development of methods to concentrate and store that energy. In this sense and inspired by biological systems, the storage of solar energy in chemical bonds is a promising alternative in the search for energy reservoirs.⁵

1.1. Artificial Photosynthesis

In nature, the photosynthetic plants have developed the most efficient energy storage process, in which sunlight is converted into accessible high energy chemicals. Thus, by mimicking that natural systems eventually it will be possible to design artificial photosynthetic systems that can employ solar energy for fuel production. The Z-scheme of natural photosynthesis shown in figure 2 can help understanding how the process of solar energy harvesting works in plants inspiring us creating more sophisticated and efficient devices.

The photosynthetic process starts with the absorption of light (photons) by a special pair of chlorophyll P680, located in the photosystem II. Once the P680 is promoted to an electronically excited state, a charge separation process takes place where an electron is transferred from a chlorophyll to an adjacent pheophytin, which transfers the

electron into an electron-transfer chain where a reducing equivalent is stored for further use. This process of charge separation give place to the formation of the strong oxidant species $P680^+$ ($E = 1.25 \text{ V vs NHE}$) that successively oxidizes the cluster $[Mn_4CaO_5]$ of the oxygen evolving-complex (OEC) activating it. In fact, four consecutive electron transfer processes (accumulation of four oxidation equivalents) to the OEC are required to yield an oxygen, O_2 , molecule and four equivalents of protons as consequence of the splitting of two water molecules. Concomitantly, the four electrons that passed through the chain of electron-transfer processes at photosystem II and I are the energy and reducing equivalents stored as NADPH and ATP for the posterior reduction of atmospheric CO_2 to carbohydrates in the Calvin Cycle.^{6,7}

Figure 2. Schematic representation of the electron transfer processes involved in photosynthesis after absorption of light and excitation of chlorophyll P680.

This way of storing chemical energy which subsequently can be released in metabolic processes, has inspired the construction of artificial photosynthetic systems for water splitting; where the electrons generated by water oxidation could either be used to reduce CO_2 to produce carbon-based fuels or to reduce protons to hydrogen. Taking into account that hydrogen is a clean fuel that only produces water during its chemical or electrochemical reaction with oxygen, and considering that the energy density of hydrogen is about 122 kJ/g , which is 2.75 times larger than that of carbon-based fuels, it has been proposed as a suitable alternative to obtain a carbon-free fuel with potential to substitute fossil fuels.^{5,8}

Considering the high complexity of the photosynthetic system, a more practical and synthetically accessible approach, have been proposed to split water (Eq. 3) and produce H_2 . Thus, this new approach requires the coupling of the two half reactions

involved in water splitting: the oxidation of two equivalents of water to generate four reducing equivalents (Eq. 1) and the proton reduction to obtain two hydrogen molecules (Eq. 2)

However, coupling those complimentary half-reactions in order to extract the stored power efficiently is not an easy task, but photosynthetic organisms does it by separating charges through a chain of electron transfer processes involving several electronically coupled compounds arranged in a suitable way in space and energy (redox potentials). Unfortunately, such a molecular device is too complicated to be reproduced yet, such that simpler photosynthetic interfaces were devised. One of them is based on the attachment of a photosensitizer (P) on a semiconductor surface (Figure 3), that upon illumination must yield a long-lived excited state capable to transfer an electron into the conduction band. This initial charge separation process is the fundamental step of photosynthesis, and generates an oxidized dye molecule P^+ that leads the oxidation of the water oxidation catalyst (WOC). The reaction of this species generating dioxygen lead to effective charge separation and regeneration of the photosensitizer. However, as in the photosynthetic system, WOC must store four oxidation equivalents by successive monoelectronic charge-transfer processes. Finally, when WOC is in its catalytic active state can abstract four electrons from water leading to O_2 evolution and concomitant release of four H_3O^+ according to (Eq. 1), as occurs in the OEC. The four electrons transferred to the semiconductor are delivered to a hydrogen evolving catalyst, which reduces the protons generated in the water oxidation to produce H_2 (Eq. 2), or eventually can be used to reduced CO_2 generating hydrocarbons, as shown in Figure 3.

Figure 3. Schematic representation of the Z-scheme of an artificial photosynthetic system including a water oxidation catalyst (WOC), a photosensitizer (P) and a hydrogen evolving catalyst (HEC). (modified from ref.9)

The reduction of protons generating hydrogen gas (Eq. 2) is fast on a platinum electrode and the overpotential tend to be low ($\Delta G_{\text{H}}^{\circ} \cong 0 \text{ eV}$). However, the oxidation of water is a more complex multiple electron and multiple proton transfer reaction (equation 1) that has been considered the bottleneck of water splitting process. In fact, there are several good catalysts for hydrogen evolution reaction,⁹ but there is a quite high kinetic barrier for oxygen evolution which arises from the multiple intermediates required to form the O-O bond, involving the simultaneous release of four protons and four electrons from two water molecules ($\Delta G^{\circ} \cong 3.72 \text{ eV}$). Thus, to overcome the highly energetic barrier of the water oxidation ($E = 1.23 - 0.059 \times \text{pH V vs NHE}$) the development of highly active and rugged water oxidation catalysts (WOCs) is necessary. In addition, they should operate under strong oxidizing conditions with a good performance and minimum deactivation/decomposition.¹⁰

1.2. Water Oxidation Catalysts

Although the replication of the OEC for its application in water splitting is extremely difficult, the constitutional nature of this complex structure has inspired the design of molecular WOCs based on transition metals and strong electron donating ligands such as O- and N-rich ligands.

1.2.1. Manganese Based WOCs

In this regard, the best characterized catalysts are based on manganese, ruthenium and iridium. Whereas manganese is the redox active metal in the OEC and significant efforts have been made to synthesize bio-inspired Mn complexes, few reports on complexes capable to catalyze the oxidation of water. Among the most significant reports is the so-called “terpy dimer” **1** developed by Crabtree and co-workers,¹¹ which drives the oxygen evolution using oxone or hypochlorite as oxidant. Also, the preparation of the Mn-corrole system **2** by Sun and co-workers,¹² that provided experimental evidence that O–O bond formation occurs via nucleophilic attack of hydroxide on Mn(V)=O species is shedding light on the mechanism of water oxidation to dioxygen, occurring at the OEC of the photosynthetic system.

Figure 4. Molecular structures of Mn-based WOCs.

1.2.2. Iridium Based WOCs

Iridium is a known heterogeneous catalyst for water oxidation, but only in 2008 Bernhard and co-workers^{6,13} reported the first family of Ir complexes, analogues of $[\text{Ir}(\text{ppy})_2(\text{OH}_2)_2]^+$ (ppy = 2-phenylpyridine) **3**, capable to mediate the oxidation of water by CAN and $\text{Ce}(\text{OTf})_4$ (TON¹ up to 2760), but at very low rates. Crabtree and co-workers¹⁴ developed a new series of complexes in order to improve the catalytic activity of these compounds, by substituting the ppy ligand by a stronger electron donating Cp* ligand (pentamethyl-cyclopentadienyl). Unfortunately, despite the enhancement of TOF²

¹ Turnover number (TON): the number of cycles for which a catalyst works before being inactivated.

² Turnover frequency (TOF) is used to refer to the turnover per time unit.

to values up to 54 min^{-1} , the complexes showed TON values lower than their analogues. In addition, the work of Crabtree was important since demonstrated that the catalyst is the molecular WOCs instead of the iridium oxides formed by oxidative decomposition of the complex.

In order to increase the stability of organometallic Ir WOCs, Bernhard and co-workers¹⁵ synthesized monomeric complexes bearing a bidentate carbene type chelate **4** and another with an abnormal pyridinium-carbene ligand NHC **5**. Interestingly, the catalysts **4** with an intermediary structure showed a good performance for water oxidation (TON=10000 vs CAN^3). According to the authors, this is because this type of ligand is able to stabilize both, the low oxidation state of the Ir complex due to its high electronic flexibility and the high oxidation state in its charge separated form.

Figure 5. Molecular structures of Ir-based WOCs.

Although relatively short time has passed since the first reports on molecular iridium precatalysts, numerous Ir-complexes have been synthesized and tested to evaluate the catalytic activity and their stability, since the iridium oxides formed by oxidative decomposition has long been recognized as heterogeneous WOCs.

1.2.3. Ruthenium Based WOCs

Ruthenium was demonstrated to be very versatile element particularly because tend to generate coordination compounds with strong metal-ligand bonds exhibiting slow ligand exchange reactions and rich electrochemical and spectroscopic properties, that facilitates the characterization and monitoring of all species, including possible transient intermediate species generated during the reactions. Such characteristics, allied to the

³ Cerium (IV) ammonium nitrate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, also known as CAN, is a strong one-electron oxidizing agent.

photochemical and catalytic/electrocatalytic properties of many of those complexes in several accessible oxidation states, facilitated mechanistic investigations providing new insights that helped demonstrate the structure-activity relationship.¹⁶ As a consequence, ruthenium based WOCs have been, by far, the most studied class of complexes for the design and development of artificial photosynthetic systems for water splitting.

In 1982, Meyer and co-workers developed the first catalyst for water oxidation, the *cis,cis*-[Ru(bpy)₂(H₂O)]₂(μ-O)⁴⁺, better known as “blue dimer” **6**. Even though the TON (ca. 13) and TOF (0.004 s⁻¹) were not impressive, it was a milestone in the field because motivated an extensive and detailed study of the complex demonstrating the feasibility and the structural requirements to realize efficient molecular multielectronic catalysts for oxidation of water. The design includes a μ-oxo bridge that favors a strong electronic coupling between ruthenium cores, thus facilitating the stabilization of the complex in high oxidation states as well as synergic interactions facilitating the oxidation of H₂O through a mechanism involving four electrons and four protons concomitantly with the formation of a O=O bond.

Scheme 1. Scheme showing a possible catalytic pathway for oxidation of water to O₂ mediated by the “Blue Dimer”, as proposed by Meyer and Co-workers. (from ref. 18, modified)

Since the synthesis of the blue dimer, some mechanisms have been proposed to explain the catalytic activity of this WOC. Among them, the most known and accepted is the mechanism proposed by Meyer, that emphasizes the role of proton-coupled electron

transfer (PCET) processes in water activation.^{6,17} According to this mechanism, the water bound to the ruthenium ion is activated upon oxidation of the metal center since decreases its pKa and promote the formation of the respective high valence hydroxo and oxo complexes. In fact, a nucleophilic attack of a H₂O molecule to the high-valence Ru^{V,V} intermediate is proposed (Scheme 1), generating the activated complex **9**, where rapidly an intramolecular electron-transfer takes place generating a superoxo complex intermediate, that release a dioxygen molecule upon an electronic rearrangement.¹⁸

After Meyer's work, for a long time, the development of new catalysts for water oxidation was directed to the synthesis of compounds analogous to the blue dimer.^{6,18} The first approach to a new class of WOCs was realized by Tanaka's group which forwarded a ruthenium complex containing the redox active ligand 3,6-tBu₂qui (3,6-di-tbutyl-1,2-benzoquinone) **11**. Because of the three redox states in which this quinone derivative (quinone, semiquinone and catechol) can exist, it was shown by comparison with a *cis*-bipyridine analogue, that the ligand can act as a reservoir of electrons during the catalytic process. The complex with the quinone group showed a higher catalytic activity than their bipyridine analogue for the generation of O₂, with the capacity to work during 40 h and reach a TON of 33500.

Figure 6. Binuclear molecular catalysts connected by robust and rigid bridging ligands, independently proposed by Tanaka's group **11**, and Llobet's group **12,13**.

Given the low stability of the μ -oxo bridge in the blue dimer leading to the dissociation of the complex into catalytically inactive species for water oxidation,^{6,19,20} new families of Ru-complexes were designed by the introduction of rigid and robust bridging ligands. Llobet and collaborators designed the [Ru₂(OH)₂(Hbpp)(tpy)₂]²⁺ complex **12** by connecting two ruthenium ions with the rigid pyrazol ligand Hbpp = 2,2'-(1H-pyrazole-3,5-diyl)dipyridine).²¹ In contrast with the blue dimer, in this case the formation of the O-O bond occurred by direct intramolecular interaction of two M-O

entities (I2M)⁴, as demonstrated by the mechanistic studies. As expected, the rate of O₂ evolution is higher in comparison with the blue dimer, inasmuch as the preorganization of the metal centers facilitates the intramolecular coupling of the two Ru^{IV}-O. However, even in optimized conditions achieved by anchoring the complex onto a solid support, the TON was as low as 250. Additional studies of a series of related complexes have shown that the substitution of the terpy in **13** by py-SO₃ ligands, can change the mechanism of O-O bond formation from an I2M to a WNA⁵ mechanism, since there is a distinct “through space interaction”. So, it was concluded from these studies that subtle variations in the ligand environment can change the mechanism from I2M to a WNA or I2M-type.

18,22

Later on, Tummel and co-workers conducted a study to determine the effect of the axial ligands on the catalytic properties of ruthenium complexes. For this purpose, they used a polypyridyl-based ligand as a bridge connecting the two ruthenium centers **14**, while varying the axial ligands.²³ The complexes obtained exhibited an improved catalytic activity with donor ligands reaching TON up to 3200. Moreover, the same study carried out with the mononuclear Ru-complex **15**, showed for the first time that mononuclear catalysts also works as WOCs, breaking the paradigm forwarded by Meyer that at least a bimetallic center is necessary to achieve efficient water oxidation catalysts. In fact, since this publication in 2005, the efforts has been focused on WOCs based on mononuclear complexes.⁸

Figure 7. Ruthenium complexes developed by Thummel and co-workers.

⁴ I2M: Interaction between two M–O entities, which can be a radical coupling or a reductive elimination.

⁵ WNA: acronym for water nucleophilic attack, where a water molecule from the solvent attacks the oxo group of the high-valence M–O moiety.

Although the complex developed by Tummel displayed large values of TON and TOF, those Ru-complexes exhibit relatively high oxidation potentials. Thus, Sun and co-workers developed a systematic study to design a complex with better catalytic activity by improving the electron donating character of the equatorial bridging ligand.

The first attempt was carried out by inserting electron donating alkyl substituents to the pyridine ligands. However, even though the catalytic activity of the complex for oxidation of water by CAN has being improved, the oxidation potentials of the resulting ruthenium complexes were not much lower than that of Tummels' WOCs. In this way, taking into account that the oxygen rich environment of the OEC helps diminishing the redox potentials of metal complexes, a carboxylate-containing ligand shown in complex **16** was designed.²⁴

The redox potentials for the couples $\text{Ru}^{\text{II,III/II,II}}$ and $\text{Ru}^{\text{III,III/III,II}}$ in table 1 display lower oxidation potential values for complex **16** in comparison with complex **14**, and improved values of TOF and TON, as expected from the inclusion of the carboxylate-containing ligand. The analogous *cis* derivative **17** showed even a better catalytic activity²⁵. In the same way the substitution of the polypyridyl groups in **14** by carboxylate moieties, resulted in the mononuclear ruthenium complex $[\text{Ru}(\text{bda})(\text{isoq})_2]$ **18**, with a TON²⁶ of 8360 and a TOF of 303 s^{-1} , comparable with the TOF of the OEC.

Table 1. Catalytic activity and oxidation potentials for complex **14**, **16** and **17**.

Complex	$E_{1/2}$ vs SCE (V)		TON	TOF (s^{-1})
	$\text{Ru}^{\text{II,III/II,II}}$	$\text{Ru}^{\text{III,III/III,II}}$		
14	1.25	1.66	538	0.046
16	0.29	0.80	1700	0.28
17	0.66	1.15	10400	1.2

Figure 8. Ruthenium complexes developed by Sun and co-workers.

The mechanism of the water oxidation reaction catalyzed by complex **18** was shown to involve noncovalent interactions of the axial ligands leading to a dimeric intermediate and radical coupling of the two $\text{Ru}^{\text{V}}=\text{O}$ units, that facilitates the formation of the O–O bond. In other words, the work of Sun and co-workers showed that even though mononuclear complexes have been used as catalyst for the tetraelectronic oxidation of water, in fact a dimeric (binuclear) activated complex was proposed indicating that the synergic coupling of two metal centers is required to achieve enhanced catalytic efficiency.

1.3. Synergistic interaction favored by bridging ligands

Taking into account the enhanced catalytic activity of WOCs with two metal centers, the *Laboratório de Química Supramolecular e Nanotecnologia* of *Universidade de São Paulo*, proposed new binuclear catalysts in which the catalytic activity of WOCs is increased by the synergistic interaction of the metallic centers through the bridging ligand.

The detailed study carried out comparing the electrocatalytic activity of the binuclear complex $[\{\text{Ru}(\text{H}_2\text{O})(\text{bpy})\}_2(\text{tpy}_2\text{ph})](\text{PF}_6)_4$ **19** and of the mononuclear species $[\text{Ru}(\text{H}_2\text{O})(\text{bpy})(\text{phtpy})](\text{PF}_6)_4$ **20** evidenced the advantages of designing catalysts with more than one metal site. Under the same experimental conditions and equivalent concentrations of ruthenium, the binuclear complex has a catalytic activity almost 20

times larger than the corresponding mononuclear counterpart, in spite of the weak coupling of the ruthenium centers.²⁷

Figure 9. Structure of the mononuclear and corresponding binuclear complex synthesized in the LQSN, whose electrocatalytic activity for water-oxidation was compared. The plot in the right shows the amount of O₂ produced as a function of time using 50 μ M and 100 μ M respectively of the binuclear **20** and mononuclear **19** complexes as catalyst. The measurement was performed in liquid phase using an oxygen detection system equipped with a Clark-type electrode employing cerium ammonium nitrate (CAN) as oxidant agent.

DFT calculations showed that the weak coupling of the ruthenium centers was in part due to the unfavorable orientation of the terpyridine rings relative to the bridging benzene ring, hindering an efficient orbital overlapping and electronic coupling. Thus, in this work we proposed a benzobisimidazole derivative as bridging ligand to improve the electronic coupling of the ruthenium complexes in the binuclear catalyst, in order to evaluate its effect on its catalytic activity for oxidation of water.

It is well known that the electronic coupling and the electron free-mean path is greatly influenced by the nature of the bridging ligand. For example, ligands containing benzimidazole moieties, as the bis(2-pyridyl)benzodiimidazole (dpimbH₂) are interesting, since it shows better π/σ donor properties than their pyridine counterparts. Particularly ruthenium complexes containing dpimbH₂ had shown a better donor character than the bipyridine based complexes. In addition, the presence of imidazole groups makes possible tuning the redox and photoelectrochemical properties of the complexes by

simple protonation/deprotonation reactions, in this way perturbing the electronic properties of the ligand. The effect of additional acid-base sites in the bridging dpimH₂ will also be evaluated, since their pK_a must be sensitive to the electron withdrawing character of the coordinated ruthenium species. For example, when water is directly coordinated, the oxidation processes takes place according to a proton coupled electron transfer (PCET) mechanism that tend to lower the potential of the oxidation reactions. This is a consequence of deprotonation that lowers the overall positive charge of the complex decreasing the intramolecular electrostatic repulsion. Following this reasoning, one can imagine that the deprotonation of the additional acid-base sites can contribute to decrease even more the total positive charge of the oxidized species, stabilizing further the high-valence species. In this way, one expects accessing even higher valence states with higher WOC activity.

II. Objective

With the purpose of contributing to the development of more efficient catalysts for oxidation of water, the aim of this work is centered in the synthesis of a binuclear complex having two covalently linked active sites, in which the electronic coupling can be tuned by the bis-bidentated dpimH₂ ligand (scheme 2), a bridging ligand exhibiting acid-base reaction sites that can be used to tune the electronic coupling and the oxidation potentials leading to formation of high-valence species, and thus the oxidation of water to dioxygen. Additionally, a molecular photocatalyst is proposed by taking advantage of the structure of the benzobisimidazole ligand, a chromophore-catalyst dyad molecule where one of two covalently linked ruthenium centers acts as chromophore and the other as active catalysts WOC.

Scheme 2. Schematic representation of the desired dinuclear complexes by employing the bis-bidentated dpimH₂ ligand. The L represent the positions of polypyridyl ligands such as tpy and bpy derivatives.

The precursor bridging ligand and its complexes were structurally characterized by CHN analysis, ESI-MS and NMR, and its electronic behavior studied by UV-Vis and electrochemical techniques.

III. Experimental Section

3.1. Synthesis

3.1.1. Synthesis of the bis(2-pyridyl)-bis-imidazole (**dpimbH₂**) ligand

The synthesis of the ligand is based on the Philips method,^{28,29} employed by Ohno *et al.*³⁰ In a two-neck round-bottom flask, 14 g of polyphosphoric acid (PPA) were added and left under vacuum and stirring at 90 °C overnight. Then 0.8 g (2.82 mmol) of 1,2,3,4-benzenetetramine tetrahydrochloride were added into maintaining a flux of nitrogen while temperature was gradually raised up to 120 °C until evolution of HCl. After the end of this reaction, 0.7 g (5.63 mmol) of 2-picolinic acid were added into and temperature was raised to 130 °C under nitrogen atmosphere. After 12 hours, the reaction mixture becomes violet and temperature was increased to 200 °C for 6 hours. The conclusion of the reaction was determined by the formation of a precipitate when an aliquot of the solution mixture was poured in water. After cooling down to 60 °C, the reaction mixture was poured into 70 mL of distilled water to obtain a violet precipitate, that was filtrated and neutralized with a sodium bicarbonate solution generating a orange-brown solid. This solid was recrystallized from a methanol-N,N-dimethylformamide 1:9 mixture to get the final purified product. Yield: 76%. CHN Analysis found: C, 56.78; H, 5.15; N, 21.55. CHN Analysis calculated for C₁₈H₁₂N₆·4H₂O C, 56.24; H, 5.24; N, 21.86. Mass spectrum: m/z = 313,4 [M-H⁺]; 314,4 [M-2H⁺].

3.1.2. Synthesis of the 4-phenyl-2,2':6',2''-terpyridine (**phtpy**) ligand

This polypyridyl ligand was prepare by following the modified Kröhnke reaction for the synthesis of substituted terpyridines.³¹ 1g (9.4 mmol) of benzaldehyde was transferred to a 250 mL round-bottom flask containing 40 mL of a 0.3 M KOH solution in ethanol. After 10 minutes of stirring at room temperature, 2.2 g (19 mmol)

of 4-acetylpyridine and 27 mL of NH_4OH 28% were added. Four hours later the formation of a precipitate in a yellow-green solution was observed. The precipitated was collected, washed once with ethanol and water, and dried under vacuum to obtain a greenish solid, which after recrystallization twice from ethanol yielded a white solid. Yield: 60 %. CHN Analysis found: C, 81.76; H, 4.99; N, 13.53. CHN Analysis calculated for $\text{C}_{21}\text{H}_{15}\text{N}_3 \cdot 4\text{H}_2\text{O}$ C, 81.53; H, 4.89; N, 13.58.

3.1.3. Synthesis of the $[\text{RuCl}_3(\text{phtpy})]$ complex

0.27 g (1 mmol) of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was transferred into a two-neck round-bottom flask of 100 mL and dissolved with 70 mL of ethanol. Then, a saturated solution 0.31 g (1 mmol) of phtpy ligand in chloroform was slowly added into the ruthenium complex solution employing an addition funnel, while keeping the temperature constant at 70 °C. After three hours of reflux, the reaction mixture was cooled to room temperature and the precipitate filtrated out and washed with water and ethanol to yield a brown solid. This solid was dispersed in hot ethanol, filtered and washed with hot ethanol to get the final product. Yield 60%. CHN Analysis found: C, 45.00; H, 3.25; N, 7.28. CHN Analysis calculated for $\text{C}_{21}\text{H}_{15}\text{Cl}_3\text{N}_3 \cdot 4\text{H}_2\text{O}$ C, 45.62; H, 3.46; N, 7.60.

3.1.4. Reduction of the $[\text{RuCl}_3(\text{phtpy})]$ complex with Zn amalgam.

The zinc amalgam was prepared by transferring granulated Zn pellets (1 eq) into a 250 mL Erlenmeyer, activating them by washing tree times with a 50% v/v aqueous HCl solution, and reacting with HgCl_2 (0.2 eq) powder in acidic solution under stirring for five minutes. The amalgamated Zn pellets were washed with distilled water until the pH was above pH 5, and finally washed with methanol and used immediately. A methanolic solution of the $[\text{RuCl}_3(\text{phtpy})]$ complex, previously purged with nitrogen gas, was added to the Zn amalgam, while bubbling nitrogen to keep an inert atmosphere and stir, until the solution color changed from brown to blue-violet as expected for the reduction of the ruthenium complex. This blue-violet solution was directly used for the preparation of the binuclear complexes.

3.1.5. Synthesis of the *cis*-[Ru(bpy)₂Cl₂] complex

This complex was prepared following the methodology employed by Meyer *et al.*³² 1g (3.82 mmol) of RuCl₃·3H₂O, 1.2g (7.68 mmol) of 2,2'-bipyridine and 1.1 g (0.26 mmol) of LiCl were refluxed in a 50 mL round-bottom flask with 20 mL of dimethylformamide, protected from light with aluminum foil. After 8 hours of reaction, the crude reaction mixture was cooled to room temperature and transferred to a 250 mL beaker with 100 mL of acetone, and kept in the refrigerator overnight. Then, the mixture was filtered to recover the product as a black solid, which was washed with water until the filtered solution becomes clear-pink, and with diethyl ether, and dried under reduced pressure in a desiccator. Yield: 60%. CHN Analysis found: C, 48.27; H, 3.42; N, 10.79. CHN Analysis calculated for C₂₀H₁₆Cl₂N₄Ru·H₂O C, 47.82; H, 3.61; N, 11.15. ¹H-NMR (300 MHz, DMSO-*d*₆) δ 9.94 (t, *J* = 10.7 Hz, 1H), 8.62 (t, *J* = 11.0 Hz, 1H), 8.46 (t, *J* = 10.8 Hz, 1H), 8.06 (t, *J* = 7.8 Hz, 1H), 7.77 (t, *J* = 6.4 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 5.5 Hz, 1H), 7.10 (t, *J* = 6.5 Hz, 1H).

3.1.6. Synthesis of [{RuCl(phtpy)}₂(dpimH₂)](OTf)₂ complex

A solution of 0.3 g (0.64 mmol) of [RuCl₃(phtpy)] was transferred to a 150 mL two-neck round-bottom flask, previously reduced with Zn amalgam and added dropwise into a solution of 0.1 g (0.32 mmol) of dpimH₂ ligand in 70 mL MeOH/H₂O 4:1 under inert atmosphere. The reaction mixture was kept at 60 °C under stirring for 6 hours, protected from light, cooled to room temperature and filtered through a sintered glass funnel. The solution was concentrated using a flash evaporator and the desired product precipitated with a concentrated aqueous lithium triflate (LiOTf) solution to obtain a dark violet solid. Given the low solubility of the solid, it was dry-loaded onto the chromatographic column by saturation of activated neutral alumina (Brockmann I) with the sample. The purification process was performed also employing activated neutral alumina (Brockmann I) as stationary phase and a DCM/MeCN/MeOH 7:2.8:0.2 mixture as eluent. The collected fractions were then purified by Silica Gel 60

column chromatography using a mixture of $\text{CHCl}_3/\text{MeOH}$ with a polarity gradient as eluent. The isolated final product was a mixture of geometric isomers. Yield 20%.

3.1.7. Synthesis of the $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)](\text{ClO}_4)_2$ complex

In order to prepare the desired complex under mild conditions, one decided to use the *aqua* complex $[\text{Ru}(\text{bpy})_2\text{Cl}(\text{H}_2\text{O})]^+$, instead of the $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ complex as reagent. 155.1 mg (0.32 mmol) of $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ was transferred to a two-neck round-bottom flask protected from light, and dissolved in 20 mL of a $\text{MeOH}:\text{H}_2\text{O}$ 1:1 mixture, and treated with 81.6 mg (0.48 mmol) of AgNO_3 solution, which was added in three portions each 15 minutes. After six hours of reaction at 60 °C, the reaction mixture was cooled in the freezer by two hours, and the solid residue (AgCl) was removed from the solution by filtration through Celite®545 bed in a sintered glass funnel. Finally, the orange-red solution was concentrated to half its volume under reduced pressure and reserved in an addition funnel for use in the synthesis.

To prepare the desired complex, the aqua complex solution was slowly added into a solution of 100 mg (0.32 mmol) of dpimH_2 in $\text{MeOH}/\text{H}_2\text{O}$ 1:9 mixture at 60 °C, under inert atmosphere and protected from light. After 8 hours the orange-brown solution was cooled to ~10 °C and filtered through Celite®545 bed in a sintered glass funnel. Then, the solution was concentrated in a rotary evaporator and precipitated with a concentrated solution of LiClO_4 . The compounds in the orange solid were initially separated by column chromatography using activated neutral alumina (Brockmann I) employing a 1:1 $\text{MeCN}:\text{Acetona}$ mixture as eluent. Two main orange colored fractions were obtained: a) one corresponding to the binuclear complex, and b) a second fraction to the desired mononuclear complex. This, fraction was purified by Silica Gel 60 column chromatography employing MeOH with 10% of a solution of LiCl (0.08% p/v) as eluent. The mononuclear complex fraction, which eluted first, was completely separated from the binuclear complex, concentrated and precipitated with a concentrated solution of LiClO_4 yielding an orange solid after drying in a desiccator under vacuum. Yield: 27%. CHN Analysis found: C, 43.48; H, 3.58; N, 12.62. CHN Analysis calculated for $\text{C}_{38}\text{H}_{28}\text{N}_{10}\text{Ru}_2(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ C, 43.44; H, 4.01; N, 13.33.

3.1.8. Synthesis of the $[\{Ru(bpy)_2\}(dpimH_2)\{Ru(phtpy)Cl\}](ClO_4)_3$ complex

In an 150 mL erlenmeyer a brown suspension of 52.7 mg (0.10 mmol) of the $[RuCl_3(phtpy)]$ complex was prepared in 20 mL of methanol mixture and treated with $Zn(Hg)$ while bubbling nitrogen, to get the reduced complex. The violet solution was slowly added (6.5 hs) into a solution of 90 mg (0.10 mmol) $[Ru(bpy)_2(dpimH_2)](ClO_4)_2$ in MeOH/H₂O 10%, at 60 °C. The resultant red wine reaction mixture was cooled to 10 °C and filtered through a Celite®545 bed in a sintered glass funnel. Then, the solution was concentrated on the rotary evaporator and precipitated by addition of a concentrated $LiClO_4$ solution. Compounds in the red wine solid was previously separated using a short column of activated neutral alumina (Brockmann I) employing a mixture of acetone/MeCN 10% as eluent. The two main violet fractions were then purified by alumina column chromatography using the same solvent, and finally by Silica gel column chromatography employing MeOH with 10% of LiCl solution (0.08% p/v) as eluent, precipitated with aqueous $LiClO_4$, washed with water and dried in a desiccator under reduced pressure. The products labeled as F1 and F2 are isomers. Yield 25%. CHN Analysis found: C, 44.02; H, 3.41; N, 11.54. CHN Analysis calculated for $C_{59}H_{43}Cl_2N_{13}Ru_{2.3}(ClO_4^-).5H_2O$ C, 44.90; H, 3.51; N, 11.54.

3.2. Instruments and Methods

3.2.1. Structural Characterization

Mass spectra were recorded in a Bruker Daltonics Esquire 3000 plus mass spectrometer. The samples were dissolved in pure N,N-dimethylformamide and diluted with methanol before injection. The ESI-MS spectrum was acquired using a capillary voltage of 4 kV.

The 1H -NMR spectra of organic molecules and small complexes were acquired in a Bruker AIII 300 MHz spectrometer, whereas the 1H -NMR and COSY 1H - 1H spectra of binuclear complexes were recorded in a Bruker DRX 500 MHz spectrometer. The

samples were dissolved in pure deuterated solvents or mixtures of deuterated solvents, in order to generate 3 mg/500 μL solution in the case of organic ligands, and 2 mg/500 μL of the ruthenium complexes. TMS was always used as internal reference.

The elemental analyses of the samples, as percentage of carbon, hydrogen and nitrogen, were recorded in Perkin Elmer 2400 series II elemental analyzer equipped with a thermal conductivity detector (TCD).

Theoretical calculations were developed by employing density functional theory (DFT) using the Gaussian 09 software. The optimized structures were calculated with the B3LYP^{33,34} hybrid functional using the SDD³⁵ basis set for the ruthenium centers and for the C, H, N, and Cl atoms the 6-31(d) basis set for the $[\{\text{RuCl}(\text{phtpy})\}_2(\text{dpimH}_2)]^{2+}$ and $[\{\text{Ru}(\text{bpy})\text{Cl}(\text{phtpy})\}_2(\text{dpimH}_2)]^{3+}$ complexes.^{27,36} After the geometric optimization of each structure frequency calculations were carry on at the same level of theory to confirm the single point is a true minima without imaginary frequencies. Appendix B shows examples of the input employed for the geometric optimization and frequencies calculations.

3.2.2. *Electronic Characterization*

The electronic spectra of the compounds in the UV-Vis region (190 nm to 1100 nm) were recorded in a Hewlett Packard 8453 spectrophotometer, employing quartz cells with an optical path of 1.00 cm.

Cyclic and differential pulse voltammetry measurements were carried out using an Autolab PGSTAT30 Potentiostat/Galvanostat, and a three-electrode electrochemical cell with a glassy carbon working electrode for measurements in MeCN or DMF solution containing 0.100 mol·L⁻¹ of tetrabutylammonium perchlorate (TBAClO₄). The employed reference electrode was Ag/AgNO₃ (0.010 mol·L⁻¹ AgNO₃) in MeCN containing 0.100 mol·L⁻¹ of TBAClO₄, and a platinum wire was used as auxiliary electrode. The potential values reported in this work were converted to the Normal Hydrogen Electrode (NHE, E = 0.000 V, [H⁺]=1) by adding 0.503 V to the experimental results.^{37,38} The pH dependence of the redox potentials was measured in CH₃CN/Britton-Robinson (BR) Buffer (1/1, v/v) 0.05M to favor the solubility of the ruthenium complexes. The pH was adjusted by adding μL s of a solution NaOH 4 M.

For the spectroelectrochemical measurement, an EG&G PAR 173 Potentiostat/Galvanostat was used in parallel with a Hewlett Packard 8453 spectrophotometer. A three-electrodes system with a high transmittance gold minigrid work electrode inside a quartz cell with restricted internal optical path length of 0.025 cm was used. A platinum wire was employed as auxiliary electrode and an Ag/Ag⁺ (0.010 mol·L⁻¹ AgNO₃) electrode in MeCN containing 0.100 mol·L⁻¹ of TBAClO₄ as reference electrode. A 0.100 mol·L⁻¹ TBAClO₄ solution in MeCN or DMF was employed as electrolyte.

IV. Discussion

4.1. Syntheses and Structural Characterization of Ligands

4.1.1. Bis(2-pyridyl)-bis-imidazole (dpimbH₂) Ligand

The synthesis of the bridging ligand was addressed from three approaches starting from the 1,2,3,4-benzenetetramine tetrahydrochloride (BTA·HCl), varying the nature of the N-heterocyclic molecule to insert the imidazole substituted moiety as shows in scheme 3.

Scheme 3. Synthetic strategies for preparation of the dpimH₂ ligand.

Initially searching for mild conditions, the one-pot methodology reported by Bahrami et. al.,³⁹ was adopted. In this case, 2-substituted benzimidazoles are prepared by the condensation of *o*-phenylenediamine with aryl-aldehydes generating a cyclic diamine fused to the benzene ring, using aqueous HCl and H₂O₂ in acetonitrile at room temperature. As shown in scheme 4, this method also relies on *in-situ* formation of hypochlorous acid (HClO) and oxidation of the cyclic diamino moiety to generate the benzimidazole ring. The electrophilic attack of hypochlorous acid lead to the formation of a N-chlorinated intermediate which eliminates a chloride and a proton oxidizing the fused ring instead of generating the respective chloramine, thus forming the imidazole ring conjugated with the benzene ring.^{40,41}

Scheme 4. Possible mechanism of synthesis of benzimidazoles from *o*-diaminebenzene, as proposed by Bahrami and co-workers.³⁵

Figure 10. ^1H -NMR spectrum (300 MHz) of a) the extracted product in $\text{DMSO}-d_6$ showing the present of a broad peak at 3.7 ppm indicating the formation of insaturated amines and the spectrum of the reagents b) BTA·HCl and c) 2-piconaldehyde in $\text{MeOH}-d_4$.

The ^1H -RMN spectra of the product (figure 10) shows a broad peak between $\delta = 3.5 - 4.0$ ppm characteristic of insaturated amines, indicating the oxidation of the cyclic aliphatic diamine generating the aromatic benzimidazole moiety. Additional attempts using the $\text{H}_2\text{O}_2/\text{CAN}$ mixture to oxidize the fused diaminepentane group, as proposed by Bharmi⁴², did not led to the formation of the desired compound.

In the pursuit for an alternative method, it was found that the modified Philips method²⁹ involving the heating of a carboxylic acid with *o*-phenylendiamine in

polyphosphoric acid (PPA)²⁸ is one of the most effective methods for carrying out cyclization reactions with a wide number of heterocyclic precursors, such as the nicotinic acid, an isomer of the 2-picolinic acid, that also allows the formation of dpimH₂. Given the viscosity and incompatibility of PPA with common solvents used in condensation reactions, the reactions conditions must be vigorous. Thus, in a first attempt, the experimental methodology reported by Wang et al.,⁴³ for the synthesis of a bridging ligand containing both imidazole and pyridine moieties, was employed.

Initially, to reduce the viscosity and favor the solubility of the starting materials, polyphosphoric acid, PPA, was heated up to 100 °C under stirring, followed by the stoichiometric addition of 2-picolinic acid and BTA·HCl, which resulted in a vigorous reaction. In agreement with the mechanism proposed by So and Heeschen,⁴⁴ the carboxylic acid is initially activated by PPA forming an ester group, which subsequently suffers a nucleophilic attack by one of the amino groups of BTA·HCl to form an amide moiety. Accordingly, after a second nucleophilic attack by the α -amino group, the dpimH₂ ligand was produced (scheme 5).

Scheme 5. Mechanism proposed for the formation of the dpimbH₂ ligand by reaction of 2-picolinic acid with BTA·HCl in polyphosphoric acid.

After heating up to 200 °C for six hours, the reaction mixture was cooled to room temperature and poured into water to deactivate PPA in the form of phosphoric acid. Then, the recovered precipitate was neutralized (pH 7) with a 5 M NaOH solution, and finally recrystallized from DMF to give a dark brown solid with 80% yield. Although this

methodology was useful, analysis of the solid by NMR and CHN methods showed the presence of some impurities, that as shown later, can cause problems in subsequent reactions where the purity of the ligand was shown to be crucial. Then, by having this procedure with PPA as condensing agent, different conditions were tried having in account the stability of the deprotonated tetramine and possible intermediates until finding the optimized methodology reported in the experimental section.

Figure 11. ^1H -RMN spectrum (300 MHz) of dpimH₂ ligand in DMSO-*d*₆. The structure of the tautomeric structures and the expanded view of spectrum in the 7.40 to 8.10 ppm is also shown.

Analysis of the ^1H -NMR spectrum of the dpimH₂ ligand (Fig. 11), allowed the assignment of the signal at 12.91 ppm to the Hc protons in the imizadole moiety, followed by the doublets between 8.75 ppm and 8.34 ppm which correspond to protons labeled as Ha and Hd. Two triplets signals attributed to the Hc and Hd protons plus three additional signals which are originated by the tautomeric equilibria of dpimH₂ in solution, are shown in the expanded view of spectrum in the 7.40 to 8.10 ppm range. As shown in the proton NMR of the respective acidified solution depicted in figure 12, the rapid exchange of protons bond to the N-atom of the imidazole ring⁴⁵ is locked due to the protonation of both N-atoms, and the Ha' and Hb' protons become equivalent.

Figure 12. ^1H -RMN (300 MHz) of the dpimH₂ bridging ligand in DMSO-*d*₆ acidified with CF₃COOD.

The analysis of the dpimH₂ ligand by ion trap mass spectrometry (Fig. 13) showed peaks at m/z 313.26 and 314.29 corresponding to the mono- and di-protonated ligand, clearly confirming the successful preparation of the bridging dpimH₂ ligand.

Figure 13. Ion trap mass spectrometry of dpimH₂ ligand showing the molecular peaks corresponding to the mono and deprotonated species.

4.1.2. Preparation of the 4-Phenyl-2,2':6',2''-terpyridine (phtpy) Ligand

The phenylterpyridine ligand was prepared following a method based on the Kröhnke³¹ reaction for the synthesis of pyridine derivatives, previously employed in the LQSN. The synthesis of the substituted terpyridine ligand is carried out under mild

conditions starting from 2-acetylpyridine and the desired aldehyde under basic conditions, as shown in scheme 6. The reaction starts upon deprotonation of the methyl moiety of acetylpyridine to obtain an enolate intermediate, which after condensation with benzaldehyde yields an α,β -unsaturated ketone. This reaction is followed by the nucleophilic addition of a second enolate through a Michael's condensation generating a 1,5-diketone derivate. Then, ammonia reacts simultaneously with both carbonyl groups of that intermediate closing a six-membered ring upon elimination of two water molecules. The central pyridine ring is finally generated upon elimination of two molecules of water and oxidation of the aliphatic cyclic amine by dioxygen, leading to the desired phenyl substituted terpyridine.

Scheme 6. Scheme of the one-pot method for preparation of the phtpy ligand starting with 2-acetylpyridine and benzaldehyde.

The first singlet at 8.75 ppm in the 1H -NMR spectrum (Fig. 14) of the phtpy ligand corresponds to the Hz proton of the central pyridine ring since it is deshielded by the ring effects of two pyridine rings at ortho positions. The double doublet at 8.73 ppm can be assigned to the Ha proton because is shifted to low fields by the ring effect of an alpha pyridyl ring. The proton Hd at 8.69 ppm appears as a double triplet since it is coupled with protons Hc and Hb. The overlapping signals between 7.92 ppm and 7.87 ppm are a doublet and a triple doublet belonging to the phenyl ring proton Ha' and the pyridyl proton Hc respectively. The remaining protons of the phenyl moiety, Hb' at 7.53 ppm appear as an overlapping triplet with the signal of Hc' at 7.47 ppm as a triple triplet. Finally, the last proton Hb of the peripheral pyridine ring appears at 7.36 ppm as a double doublet of doublets.

Figure 14. ¹H-RMN spectrum (300 MHz) of phtpy ligand in CDCl₃ solution. The different protons in the structure are indicated in the structure for clarity.

4.2. Strategies to prepare the [{RuCl(phtpy)}₂(dpimbH₂)](OTf)₂ complex

The synthesis of the binuclear complex [{RuCl(phtpy)}₂(dpimbH₂)](OTf)₂ which present two adjacent active sites for oxidation of water, was approached by different synthetic methods given the unexpected drawbacks in its preparation. Such approaches were classified according to the reducing agent employed in the synthesis.

4.2.1. Reduction with organic amines

Once the ruthenium complex [RuCl₃(phtpy)] was prepared by following the procedure previously described in the methodology section, it was established a first approach to the synthesis of the *cis*- and *trans*-[{RuCl(phtpy)}₂(dpimH₂)]²⁺ complexes using the experimental conditions reported in the literature,²¹ and procedures previously employed in the group, for the preparation of binuclear complexes containing terpyridine and analogous ligands.

The conditions initially employed in the synthesis are summarized in scheme 7, in which the reduction of the Ru(III) to the Ru(II) complex by 4-ethylmorpholine (NEM) was expected, thus facilitating the dissociation of the chloride ions from the $[\text{RuCl}_3(\text{phtpy})]$ complex to allow the binding of the dpimbH_2 ligand; whereas LiCl was used to prevent the dissociation of the chloride ligand from the product.

Scheme 7. Initially chosen route for the synthesis of the desired binuclear $[\text{RuCl}(\text{phtpy})]_2(\text{dpimbH}_2)]^{2+}$ complexes.

The UV-Vis spectrum of the reaction mixture recorded after three hours of reflux (Fig 15), showed the absorption bands centered in the phtpy ligand shifted from 253 nm and 290 nm to 290 nm and 320 nm, the bands of the bridging dpimbH_2 ligand shifted from 351 and 368 nm to 382 and 406 nm, and the overlapping bands between 490 and 600 nm attributed to metal-to-ligand charge-transfer transitions. Purification of the crude product by column chromatography (CC) led to five fractions that behaved as single compounds during the purification process.

Figure 15. UV-Vis spectrum of the crude reaction mixture of the first preparation attempt in DMF, compared with the spectrum of the dpimbH_2 and phtpy ligand, and of the $[\text{RuCl}_3(\text{phtpy})]$ complex in the same solvent. The spectra were normalized following the spectrum of the free phtpy ligand.

As shown in the spectra of the main fractions separated by column chromatography (figure 16), the spectroscopic profiles of the fractions C, D and E are very similar, since all three presents the phtpy and dpimH₂ ligands intraligand bands expected for the $[\{RuCl(phtpy)\}_2(dpimH_2)]^{2+}$ complex, as well as the MLCT bands indicating the coordination with ruthenium(II) ions. However, fractions A and B displayed totally different spectral profiles, characterized by the lack of the band belonging to the bridging ligand and the presence of a sharp MLCT band. Nevertheless, the fraction B was isolated as an orange solid with a yield of 54%.

Figure 16. UV-Vis spectrum of representative fractions obtained by alumina column chromatography (eluent: Acetone/MeCN) of the crude sample from the first attempt for preparation of the binuclear complexes.

Analysis of the fraction B by UV-vis (figure 16) and ¹H-RMN (figure 17) showed that under the experimental conditions employed, the equilibria of the reaction was shifted to yield the bisterpyridine complex $[Ru(phtpy)_2]^{2+}$ as the major product. This was an unexpected result since the bridging bis-bidentate ligand 2,6-bis(2-pyridil)bezodiimidazole (dpimbH₂) has strong σ donor properties, and is known to stabilize binuclear complexes after reaction with $[Co(bpy)_2Cl_2]$, $[Rh(bpy)_2Cl_2]$, and $[Ru(bpy)_2Cl_2]$ complex.^{30,46} In fact, as we will show afterwards, it is possible to obtain the desired binuclear complexes, starting with $[Ru(bpy)_2Cl_2]$ and $[Ru(phtpy)Cl_3]$ complexes.^{30,46}

Figure 17. ^1H -RMN (300 MHz) of the $[\text{Ru}(\text{phtpy})_2](\text{ClO}_4)_2$ complex in $\text{DMSO}-d_6$.

On the other hand, the analysis of the fractions C, D and E by TLC showed a mixture of two or three compounds in each fraction, in contrast with the main products expected initially; i.e. two geometric isomers (*-cis* and *-trans*) as a function of the position of the phtpy ligand and a mononuclear complex. Looking for an explanation for the larger number of compounds found by TLC, we realize that the geometry of our bridging ligand could allow the formation of several geometric isomers depending on the relative position of the $-\text{Cl}$ ligand in the structure of the binuclear complex. The optimized structure and calculated energy by DFT (B3LYP) for each isomer are shown in figure 18, as well as the total electronic energy. It is easy to observe that given the low energy differences between them, at least in theory, all structures could be formed during the synthesis of the binuclear complex.

Analysis by low resolution electron spray ionization mass spectrometry (ESI-MS) of the fractions C, D and E from the first preparation attempt to obtain the desired binuclear complexes, indicated the formation of a single peak centered in m/z 755.26 ($\Delta m/z = 1.0$) which was assigned to the mononuclear species $[\text{RuCl}(\text{phtpy})(\text{dpimbH}_2)]^+$. It was believed that the formation of the homoleptic complex $[\text{Ru}(\text{phtpy})_2]^{2+}$ generates a stoichiometric imbalance between the bis-bidentate bridging ligand dpimH_2 and the $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ complex that impairs the formation of the binuclear complex.

Figure 18. Possible geometric isomers for the $[\{\text{RuCl}(\text{phtpy})\}_2(\text{dpimH}_2)]^{2+}$ complex, and respective total electronic energy.

In order to explain the unexpected result of this synthesis, two hypotheses were raised: a) free phtpy ligand present as impurity of the $[\text{RuCl}_3(\text{phtpy})]$ complex lead to the formation of the homoleptic bis(terpy) complex, or b) the high temperature and the large excess of LiCl led to dissociation of the phtpy ligand from the $[\text{RuCl}_3(\text{phtpy})]$ complex generating the free phtpy ligand responsible for the formation of $[\text{Ru}(\text{phtpy})_2]^{2+}$ complex. The first hypothesis was discarded because, as it will be shown later, free phtpy was not found in the $[\text{RuCl}_3(\text{phtpy})]$ complex used as reactant. The several attempts/strategies employed to avoid the formation of bis(terpy) complex as the main product are summarized in Table 2. The approaches include variations in reaction conditions, solvents and stoichiometry of reagents, in addition to attempts carried out using complexes such as $[\text{RuCl}_2(\text{H}_2\text{O})(\text{phtpy})]$ and $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$. However, no one was fruitful.

Table 2. Representative experiments carried out for preparation of complexes $[\{\text{RuCl}(\text{phtpy})\}_2(\text{dpimbH}_2)]^{2+}$, with a 2:1 stoichiometric ratio relative to $[\text{Ru}^{\text{III}}(\text{phtpy})\text{Cl}_3]$ complex and the ligand dpimbH_2 .

Solvent	Eq. LiCl	Temperature ($^{\circ}\text{C}$)	Time (hours)	Reducing Agent
DMF/ H_2O	10	150	4	NEM
DMF/ H_2O	3	70	0.5	NEM
DMF*	0	54	2	NEM
EtOH/ H_2O	3	40	6	TEA
EtOH/ H_2O	3	R.T.	19	TEA
EtOH	0	37	12	TEA
MeOH/ H_2O **	1.5	80	2	TEA

*Using the aqua complex $[\text{RuCl}_2(\text{H}_2\text{O})(\text{phtpy})]$

**Slow addition of $[\text{RuCl}_3(\text{phtpy})]$ to the reaction mixture.

After all those many attempts, we recognized that possibly the $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ precursor complex is in fact releasing the phtpy ligand during the reaction, leading to the formation of the homoleptic $[\text{Ru}(\text{phtpy})_2]^{2+}$ species and solvated RuCl_3 . To prove this hypothesis, a methanolic solution of $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ under stirring at room temperature, was monitored by UV-Vis spectrophotometry. To our delight, after some hours, the formation of the homoleptic bis(phtpy) complex was confirmed by the rise of a characteristic band at 490 nm (Fig 19). However, this is demonstrating that the Ru^{III} -phtpy bond is unexpectedly labile going against a strongly established believe on the inertness of $\text{Ru}(\text{III})$ complexes, particularly when involving tridentated ligands such as terpyridine. Considering these results, one decided to explore an alternative preparation strategy based on the reduction of the $[\text{Ru}^{\text{III}}(\text{phtpy})\text{Cl}_3]$ complex to $[\text{Ru}^{\text{II}}(\text{phtpy})\text{Cl}_3]$ in this way increasing the stabilizing back-donation interactions, before reacting with the bridging bis-bidentate ligand dpimbH_2 .

Figure 19. UV-Vis spectrum of the $[\text{RuCl}_3(\text{phtpy})]$ complex solution in DMF containing LiCl (3 eq) and 4-ethylmorpholine after stirring for ten minutes.

4.2.2. Reduction of $[\text{Ru}^{\text{III}}(\text{phtpy})\text{Cl}_3]$ complex with Zn(Hg)

Accordingly, the preparation method was changed by first reducing our intermediate complex to $[\text{Ru}^{\text{II}}(\text{phtpy})\text{Cl}_3]^-$ using Zn(Hg) amalgam under N_2 atmosphere, since ruthenium(II) is known to form thermodynamically more stable complexes with N-heterocyclic ligands such as terpy derivatives, while weakening the bond with the chloro ligands, thus hindering the undesired dissociation reaction and favoring the formation of the expected binuclear complexes. Once the reduction of the ruthenium complex was completed, it was added in a methanolic solution of dpimbH₂ and stirred at 50 °C, under N_2 atmosphere.

After eight hours, the UV-Vis spectrum of the reaction mixture did not change anymore and show no evidence of formation of the homoleptic $[\text{Ru}^{\text{II}}(\text{phtpy})_2]^{2+}$ complex (Fig. 20). However, a more careful evaluation by TLC and by column chromatography evidenced the formation of the bis(terpyridine) complex in about 10% yield. On the other hand, the UV-vis spectra of the main fractions shown in the figure 20 were similar and all exhibited shifted phtpy and dpimH₂ intra-ligands absorption bands, as well as the metal-to-ligand charge transfer band in the visible that evidence the formation of the desired complexes. In comparison with the former methodology employing organic reducing agents, one achieved to decrease the yield of the homoleptic bis(terpyridine) complex and the formation of the binuclear complex, as demonstrated by the mass spectroscopy

analysis. However, as expected, the main fractions were shown to be a mixture of ruthenium complexes.

Figure 20. UV-vis spectrum in MeOH solution of the crude mixture obtained upon reaction of $[\text{Ru}^{\text{II}}(\text{phtpy})\text{Cl}_3]$, generated by reaction with Zn(Hg) amalgam under N_2 atmosphere, with dpimH₂ as compared with the UV-vis spectra of free dpimH₂ and phtpy ligands (left); and UV-Vis spectra of the main fractions separated by column chromatography (right).

Analysis of the main fractions by ESI-MS is shown in figure 21. All of them exhibit a very strong molecular peak centered at m/z 1203 ($\Delta m/z = 1$) which correspond to the monoprotonated ion complex $[\{\text{RuCl}(\text{phtpy})\}_2(\text{dpimH})]^+$, and the isotopomeric pattern correspondent to the seven ruthenium isotopes ^{104}Ru (18.7%), ^{102}Ru (31.6%), ^{101}Ru (17.0%), ^{100}Ru (12.6%), ^{99}Ru (12.7%), ^{98}Ru (1.88%), and ^{96}Ru (5.52%). These are clear indication of quite pure samples of the binuclear species. Furthermore, from the spectra in figure 21 the fractions collected presents common peaks. Analysis by Tandem Mass Spectrometry (MS/MS) of the molecular ion at m/z 1203.2 ($\Delta m/z = 1$) yields peaks at m/z 446 ($\Delta m/z = 1$) and at m/z 758 ($\Delta m/z = 1$) which are associated with the fragmentation of binuclear complex yielding the monocationic species $[\text{RuCl}(\text{phtpy})(\text{dpimH}_2)]^+$ (MW = 758) and $[\text{RuCl}(\text{phtpy})]^+$ (MW = 446). Since the MS/MS analysis of the molecular ion did not show the presence of peaks at m/z 410.1 and m/z = 310.2, it is possible that the first main fraction (Fig. 21) contains free phtpy ligand, which is corroborated by the intense absorption bands characteristic of that species in the 310 to 340 nm range (Fig. 20).

Figure 21. ESI-MS spectrum of column chromatography fractions A, B and C showing the molecular peak correspondent to the binuclear $[\{RuCl(phtpy)\}_2(dpimH)]^+$ species. The inset displays an expanded view of the isotopic distribution of the m/z 1203.2 peak.

Figure 22. Monocationic species corresponding to the molecular ion and generated by fragmentation of the $[\{RuCl(phtpy)\}_2(dpimH)]^+$ complex registered by ESI-MS and tandem MS/MS spectrometry.

4.3. Electronic Spectroscopy and Electrochemistry

4.3.1. *dpimH₂ free ligand*

The electronic properties of bis-bidentate benzobisimiladozole bridging ligand is dependent on its protonation state. Thus, a spectrophotometric titration was carried out in order to know how the energy levels, and consequently the spectral profile of the ligand, are changed by protonation state and determine the pK_a values associated with the respective acid-base equilibrium.

A 3×10^{-5} mol.dm⁻³ solution of the dpimH₂ ligand was prepared using a 0.5 mol.dm⁻³ NaCl solution in MeOH/H₂O 1:3 v/v mixture, the initial pH was adjusted to pH=13 and acidified with a 8 mol.dm⁻³ HCl solution, to maintain the volume more or less constant, while registering spectra as a function of pH. The spectrum at pH 2.0, 7.1 and 12.0 are shown in Figure 23. The pK_{a1} = 2.14, assigned to the dpimH₂/dpimH⁻ acid-base equilibrium, and pK_{a2} = 10.62, corresponding to the dpimH⁻/dpim²⁻ process, were determined upon analyses of the set of titration curves. Furthermore, the deprotonation of

the dpimH₂ ligand induced a bathochromic shift of the π - π^* bands at 350 nm as expected for the more pronounced shift of the HOMO π -orbital to higher energies, whereas the band arising at 425 nm was assigned to a n - π^* transition.

Figure 23. UV-vis spectra of the dpimH₂ ligand at pH 2.0 (blue line), pH 7.1 (red line) and pH 12.0 (black line) in MeOH/H₂O 1:3 v/v mixture.

The CV and square wave voltammogram of the free dpimH₂ ligand in DMF, using a glassy carbon electrode is shown in figure 24a. The two irreversible oxidation waves with anodic peaks at E_{ap} =0.60 V and 0.92 V was assigned to the formation of cationic mono radical and the dication. Those oxidation processes probably involve the removal of an electron from the -NH imino moieties, thus affecting the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. However, no significant changes could be observed in the π - π^* transition (350 nm) and a small decrease and broadening, similar to that observed in the fully protonated species, were observed in the spectroelectrochemistry profile in the 0.34 to 1.20 V (figure 24b) range. A possibility to improve the results is changing the solvent, but this was precluded by the low solubility of the ligand, that did not allow the use of a different solvent.

Figure 24. Cyclic voltammograms of free dpimH₂ ligand in DMF solution using a glassy carbon electrode (a), and respective spectroelectrochemical behavior in the 0.34 to 1.20 V, -0.20 to -0.73 V, and -0.73 to -1.26 V range (b-d). 0.10 M TBAClO₄ solution in DMF was used as electrolyte.

Two irreversible waves were also observed in the cathodic sweep in the 0.0 V to -1.56 V range. The first irreversible process at -0.50 V can be assigned to the formation of hydrogen gas by reduction of ligand's protons. In fact, a similar shift of the π - π^* transition was observed but the band was found at 400 nm (figure 24c) instead at 490 nm (figure 23), as observed in the spectrophotometric titration. Furthermore, there is no signal of the n - π^* transition at 425 nm suggesting that the species generated upon reduction at -0.73 V may be different from the deprotonated ligand. However, those differences may be consequence of solvent effect (DMF was used in the spectroelectrochemistry). This assumption was supported by the fact that the reduction wave at -0.50 V was significantly enhanced when Pt electrode was employed instead of the GC electrode. The second reduction process at $E_{pc} = -1.13$ V probably is associated with the reduction of the dpimH⁻ to the dpim²⁻ species. The spectroelectrochemical profile for these reduction reactions, shown in the figure 24d, exhibited a small bathochromic shift of the $\pi \rightarrow \pi^*$ transition at 400 nm and the intensification of the n - π^* band at 425 nm, that now appears clearly as a

shoulder. More interesting spectroelectrochemical behavior was observed for the ruthenium complexes, as described below.

4.3.2. Binuclear $[\{RuCl(phtpy)\}_2(dpimH_2)](Otf)_2$ complex

Two successive cyclic voltammograms of the $[\{RuCl(phtpy)\}_2(dpimH_2)](Otf)_2$ complex in acetonitrile solution, using a glassy carbon electrode, is shown in figure 25a. The first scan (black line) displays a reversible anodic peak at 0.72 V that can be attributed to redox processes associated with two Ru^{3+}/Ru^{2+} pair with the same (or very similar) potentials. This behavior is evidence of a weak coupling between the ruthenium centers in the diprotonated complex. Analysis of the second anodic peak at 1.34 V at different scans rates, in the 20 mV/s to 100 mV/s range (inset Fig. 25a), showed a significant current enhancement accompanied by a shift to more positive potentials as a function of the scan rate, as expected for a diffusion limited process with significant resistance for heterogeneous charge-transfer. Considering the oxidation of the $dpimH_2$ ligand in the anodic region, this behavior can be associated with a catalytic oxidation of the solvent involving the $dpimH_2$ ligand radical cation.

The region in the 0.00 V to -1.57 V range displays three cathodic processes. The first one at $E_{cp} = -0.67$ V can be assigned to the evolution of hydrogen upon reduction of the $dpimH_2$ ligand. The corresponding reduction process in the free ligand (-0.50 V) is 170 mV shifted to more negative potentials, as expected for a reduced acidic character of the -NH protons of the ligand coordinated to Ru(II) species as a consequence of a significant back-bonding interaction. The next two anodic peaks at -1.10 V and -1.36 V can be attached to the second reduction of the ligand and the reduction of the $phtpy$ ligands.

It is remarkable from the CV in figure 25a that before the end of the first scan a second anodic peak at 0.41 V emerged in the voltammogram, the peak at 1.38 V is shifted to 1.28 V in the second scan and the current of the anodic peak at -0.69 V increased in the second scan. In view of this particular behavior, to analyze the dependence of each peak with other, and correlate them with a particular process and to evaluate better its reversibility, the CV of the binuclear complex was registered in different potential windows as shown in the figure 25b.

Figure 25. (a) Cyclic and differential pulse voltammograms of the binuclear $[\{RuCl(phtpy)\}_2(dpimH_2)](Otf)_2$ ($1\text{ mmol}\cdot\text{dm}^{-3}$) complex in MeCN using a glassy carbon electrode in the -1.6 to 1.6 V range, and at different scan rates in the -0.05 to 0.6 V range (inset); and b) CV's in different potential windows in the -1.6 V to 1.73 V range. The solid (—) and dashed (----) lines correspond to the first and second scan respectively.

From the top to the bottom in the Fig. 25b, the profile of the anodic peaks in the 0.0 V to 1.7 V range remained more or less constant, including in the second scan. Therefore, those changes must be related with the redox processes involving the ruthenium ion and the coordinated ligands. On the other hand, the peaks in the 0.0 V to -1.6 V range can be assigned to complex reduction processes. In particular, the wave at -0.69 V, that increased in the second scan, was assigned to the reduction of a ligand in the complex coupled with the formation of hydrogen.

The analysis of the CV in the -0.95 V to 0.94 V (the third CV in Fig.25b) showed that the first reduction of the bridging ligand induced the emergence of an anodic peak at 0.42 V. Considering that the deprotonation of the bridging ligand took place at that potential (-0.69 V), the new anodic peak can be assigned to the oxidation of the deprotonated species whose potential is decreased because the conjugated base is a much stronger σ -donor than the protonated ligand. On the other hand, the expansion of the window from -0.95 V to 1.7 V shows that the oxidation potential of the dpimH₂ ligand is also shifted to lower potentials and found at 1.38 V.

The spectroelectrochemical behavior in the 0.54 V to 1.04 V range is shown in figure 26a. The decay of the metal-to-ligand charge transfer (MLCT) band at 535 nm is characteristic of the oxidation from a ruthenium(II) to a ruthenium(III) complex, that also affects the bands belonging to the internal transitions ($\pi \rightarrow \pi^*$) of the phtpy and dpimH₂ ligands at 284 nm and 361 nm, that appear as a bathochromic shift and slightly decrease with the concomitant rise of a band in 303 nm. The profile of the bridging ligand bands after the oxidation of the ruthenium ion is similar to that of the free ligand at pH 7.09 (Fig. 23), which means that probably the compound is being deprotonated due to the increased acidity of the -NH group in the Ru^{III}Ru^{III} species. The inset in the figure 26a, shows that the fading of the MLCT band is followed by the growth of a band in 792 nm that may be assigned to a LMCT band considering the relatively strong donor character of the deprotonated bridging ligand. At potentials above 1.04, where the catalytic oxidation of the solvent is observed, the intensity of all absorption bands decreased indicating the decomposition of the binuclear complex (Fig. 26b).

Figure 26. Spectroelectrochemical behavior of the $[\{RuCl(phtpy)\}_2(dpimH_2)](Otf)_2$ complex during the oxidation in the 0.54 to 1.64 V range.

The spectroscopic behavior of the binuclear $[\{\text{RuCl}(\text{phtpy})\}_2(\text{dpimH}_2)](\text{Otf})_2$ complex during the reduction in the -0.6 to -1.6 V range is shown in Fig. 27. As seen in the CV of the complex (Fig 25), the reduction of the bridging ligand in the -0.65 to -1.00 V (Fig. 27a) range lead to the bathochromic shift and decay of the intraligand $\pi \rightarrow \pi^*$ transitions at 362 nm that correspond to the dpimH₂. A similar behavior was observed for the free dpimH₂ ligand when it was deprotonated upon pH increase of the solution (Fig. 23). The concomitant decay of the bands at 284 and 383 nm belonging to the phtpy ligands internal transitions suggests that the cathodic waves for the reduction of both ligands is superimposed and coupled with the reduction of H⁺ to H₂. Berger and McMillin⁴⁷ showed that the one-electron reduction of mixed-ligand complexes involves introducing an electron into a π^* orbital that is essentially localized on the tpy ligand system, and that upon the first reduction of the complex the MLCT band is split in new bands. The absorbance decrease of the MLCT band at 533 nm and the rise of the shoulder at 450 nm and the band at 594 nm, can be associated with the introduction of an electron into the π^* orbital of one of the phtpy ligands.^{48,49}

Figure 27. Spectroelectrochemical behavior of the $[\{\text{RuCl}(\text{phtpy})\}_2(\text{dpimH}_2)](\text{Otf})_2$ complex during the reduction of the ligands in acetonitrile solution.

A significant increase of absorbance of the bands below 297 nm, where the $\pi \rightarrow \pi^*$ transitions of the terpyridine ligands and internal transitions of the dpimH₂ ligand are found, were observed in the -1.00 to -1.20 V range (Fig. 27b). In general, the intensity of all absorption bands increased suggesting the formation of a new reduced species. Finally, going to the end of the CV, in the -1.20 V to -1.56 V range (Fig. 27c), the spectral profile changed once again suggesting another reduction process associated with the reduction of the second phtpy ligand in the complex and disappearance of the 330 nm band. It is also notable the concomitant intensification of the MLCT band upon reduction of the second phtpy ligand, that can weaken the π -backbonding interaction of the bridging ligand with the ruthenium centers.

4.3.3. Redox-pH dependence of the $[\{RuCl(phtpy)\}_2(dpimH_2)]^{2+}$ complex

An additional exploratory study was realized to envisage the effect of pH in the 2.0 to 9.0 range on the electrochemical behavior of the symmetric binuclear $[\{RuCl(phtpy)\}_2(dpimH_2)]^{2+}$ complex. The cyclic voltammograms were registered using a glassy carbon electrode and the complex dissolved in CH₃CN/BR buffer 1/1 (v/v) solution. As shown in figure 28, the solution pH has a significant effect on the redox potential of the dinuclear complex due to the presence of -NH groups amenable to acid-base reaction in the imidazole moieties of the dpimH₂ bridging ligand. Notice that this group is the only possible acid-base site since the sixth positions are occupied by pyridine and chloro ligands. When the pH of the buffer solution was increased from 2 to 8, the CVs were continuously shifted to less positive potentials by ~50 mV for pH unity. This negative displacement, as discussed before, is consequence of the deprotonation reaction coupled to the redox process, in other words, the oxidation of Ru(II) complex to Ru(III) increase the acidity of the benzoimidazole group that deprotonates generating the respective conjugated base of the dpimH₂ ligand with enhanced σ -donor ability. The redox potential stop shifting when the solution pH become equal or superior to pK_a(III), i.e. the pK_a of the oxidized Ru(III) species.

However, it is evident that the electrochemical behavior starts to change for pH's larger than 6.1 where two waves starts to be clearly defined. A more careful inspection is necessary to see that the apparently single pair of waves at low pH's is in fact constituted

by two reversible waves with similar redox potentials. In fact, a small broadening of the waves, especially of the reduction wave, is noticeable. This suggests a weak but significant electronic interaction between the ruthenium sites through the dpimH₂ bridging ligand. However, the electronic coupling seems to be significantly enhanced with the deprotonation one of the imidazole –NH groups as demonstrated by the presence of two well defined redox processes separated by 140 mV. Interestingly enough, the less positive wave was shifted upon pH increase indicating that there still is one protonated imidazole –NH group susceptible to acid-base reaction coupled to the oxidation process responsible for the redox potential shifting.

Figure 28. Cyclic voltammograms at pH = 2.2, 3.3, 4.2, 5.1, 6.1, 7.2 and 8.1 in CH₃CN/BR buffer (1/1, v/v) using a glassy carbon electrode, at scan rate of 100 mV s⁻¹ (a) and half-wave potential (E_{1/2}) as a function of the pH value (Pourbaix diagram) (b) of the dinuclear [{RuCl(phtpy)}₂(dpimH₂)]²⁺ complex.

From the series of CV collected in figure 28, is also observed that at pH 7 the wave with intensity corresponding to the transfer of one electron per ruthenium site splits into two one-electron waves at 0.54 V and 0.40 V which can be attributed to each one of the ruthenium centers in the binuclear complex. In the pH range from 7 to 9, the redox potential of one of the Ru centers stay constant, whereas the other is still shifted as a function of pH, suggesting that the first pK_a of the Ru^{II}Ru^{II} complex is probably around pH 6 and 7. The analysis of the dinuclear complex in the pH 8 to 9 by DPV displayed additional waves that could be assigned to the species generated upon chloride exchanges in basic media. Preliminarily, this behavior suggests that the electronic coupling between the ruthenium centers is enhanced by the formation of the monoprotonated [{RuCl(phtpy)}₂(dpimH⁺)] complex, a property that eventually could allow the tuning of the electronic and catalytic properties of the complex.

4.4. Syntheses and structural characterization of the mononuclear $[\text{Ru}(\text{bpy})_2(\text{dpimbH}_2)](\text{ClO}_4^-)$ and binuclear $[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}](\text{ClO}_4^-)_3$ complexes

4.4.1. Preparation of the Mononuclear $[\text{Ru}(\text{bpy})_2(\text{dpimbH}_2)]^{2+}$ Complex

The synthesis of the mononuclear $[\text{Ru}(\text{bpy})_2(\text{dpimbH}_2)]^{2+}$ complex was carried out by slow addition of 1 equivalent of the aqua complex $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})\text{Cl}]^+$ complex into a free dpimH₂ ligand solution in 1:1 MeOH:H₂O mixture and reflux for 6 hours. The color of reaction mixture changed from wine red to orange indicating the consumption of the dichloro derivative and formation of the desired complex. After purification, two main fractions belonging to the mononuclear and the binuclear ruthenium complexes were identified by UV-vis spectroscopy. The spectral profiles of both compounds are similar but there are two significant differences that allow the assignment of each spectra, as shown in figure 29, despite the high similarity of the bpy π - π^* intraligand bands. First, the band of the bis-bidentate dpimH₂ ligand in the 350 to 400 nm range is bathochromically shifted in the binuclear complex because the bonding of the second metallic center tends to stabilize the π^* level of dpimbH₂ ligand.⁵⁰ Also, the relative intensity of the dpimH₂ π - π^* intraligand band is larger in the mononuclear complex as compared to the bpy band at 288 nm, because the bpy/dpimH₂ ratio increase from 2:1 in the mononuclear complex to 4:1 in the binuclear complex. Despite the significant change observed in the dpimH₂ intraligand band, the envelope of metal-to-ligand charge transfer bands at 460 nm is only slightly red shifted in the binuclear as compared to the mononuclear complex.

Figure 29. UV-vis spectra of the mononuclear $[\text{Ru}(\text{bpy})_2(\text{dpimbH}_2)]^{2+}$ and the binuclear $[\{\text{Ru}(\text{bpy})_2\}_2(\text{dpimbH}_2)]^{4+}$ complex in MeOH solution normalized with the band at 290 nm.

Once the desired column chromatography fractions were identified and purified, the complexes were characterized by Electro Spray Ionization Mass Spectrometry (ESI-MS, Fig. 30). As expected, the mononuclear ruthenium complex demonstrated to be quite stable and only a strong molecular peak centered at m/z 725.06 ($\Delta m/z = 1.0$), and a much weaker signal at 362.86 ($\Delta m/z = 0.5$), respectively assigned to a monocationic and bicationic species, were found in the spectrum. Considering that one $[\text{Ru}(\text{bpy})_2]^{2+}$ group was coordinated by a dpimbH_2 ligand, the benzimidazole N-atom in the opposite side must be protonated to generate the biprotonated $[\text{Ru}(\text{bpy})_2(\text{dpimbH}_2)]^{2+}$ species in the gas phase. On the other hand, the monocationic species can be assigned to the $[\text{Ru}(\text{bpy})_2(\text{dpimbH})]^+$ complex coordinated to the monodeprotonated dpimbH^- ligand. As shown in the inset, both species exhibit isotopomeric patterns that are in good agreement with the calculated patterns considering the presence of seven ruthenium isotopes ^{104}Ru (18.7%), ^{102}Ru (31.6%), ^{101}Ru (17.0%), ^{100}Ru (12.6%), ^{99}Ru (12.7%), ^{98}Ru (1.88%), and ^{96}Ru (5.52%) whose natural abundance is indicated in parentheses.

Figure 30. ESI-MS spectra of the mononuclear $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)](\text{ClO}_4)_2$ complex showing molecular peaks corresponding to the $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)]^{2+}$ (m/z 362.86) and $[\text{Ru}(\text{bpy})_2(\text{dpimH})]^+$ (m/z 725.06) species.

The structural analysis of the mononuclear complex by ^1H -RMN (Fig. 31) allows the identification of dpimH_2 , bpy and phenyl protons in 26 different magnetic environments, but the signals corresponding to the NH in the imino moieties did not appear in the spectrum probably because of the fast exchange rate. The assignment of such a large number of signals is quite difficult and require a strategy. In our case, the signal at 8.68 ppm (d, $J=4.9$ Hz) was used as reference since it is characteristic of the α -pyridyl protons in the free dpimH_2 ligand.

The low symmetry around the metallic nucleus is reflected on the number of signals in the spectra (20 signals). Thus, the ^1H - ^1H COSY homonuclear correlation spectrum and the spectrum of complexes with similar structures⁵¹ were used as comparison to realize the complete assignment of all ^1H -RMN peaks. The analysis of the bidimensional COSY spectra allowed the identification of the correlated signals corresponding to the six pyridyl rings. Also, the signals at 11.35 ppm and 6.05 ppm were found not to be correlated with any other protons, and thus were assigned to the benzene ring Ha' and Hb' protons. The integral of these signals can vary depending on the acid-base equilibria involving the proton exchange in the N-H groups of the imidazole moieties, as discussed before. The proton Ha' is shifted to lower field, whereas the Hb' is shifted to high field because of the ring current effect felt by this proton which is facing the center of pyridine 6 ring of the complex.

Figure 31. ^1H -NMR spectrum and structure of the mononuclear $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)](\text{ClO}_4)_2$ complex in acetonitrile- d_3 , and the expanded views in three relevant spectral regions.

The alpha pyridyl protons around the ruthenium center, were identified by their coupling constants, 5.8 Hz for the bipyridine ligands and 4.9 Hz for the pyridine in the dpimH₂ ligand, taking as reference the J-coupling of the alpha protons in the $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ complex ($J = 5.3$ Hz) and in free dpimH₂ ligand ($J = 4.7$ Hz). Considering the molecular geometry around the ruthenium ion, the ligands are perpendicular to each other, and as happen with the proton Hb', these protons are located above the pyridine ring of the adjacent ligand and thus are shifted to higher fields by ring current effect.⁵²

Identification of the alpha pyridyl protons in dpimH₂, allows the assignment of the remaining protons in the ligand. In the bipyridine ligands, this assignment was performed starting with the chemical shifts reported for the analogous benzimidazole complex [Ru(bpy)₂(pbimH)](PF₆⁻)₂ in which pbimH is a bidentate ligand.⁵¹

4.4.2. Binuclear [$\{Ru(bpy)_2\}(dpimH_2)\{Ru(phtpy)Cl\}\}(ClO_4)_3$ Complex

After preparing the mononuclear [Ru(bpy)₂(dpimH₂)](ClO₄)₂ complex, we proceeded with the synthesis of the binuclear [$\{Ru(bpy)_2\}(dpimH_2)\{Ru(phtpy)Cl\}\}(ClO_4)_3$ complex as follow. The intermediate [Ru(phtpy)Cl₃] complex was prepared according to a procedure described in the literature, by reaction of RuCl₃ hydrate and phtpy ligand in refluxing EtOH. Then, a dispersion in deaerated methanol was previously reduced with Zn(Hg) amalgam and the resultant solution slowly added into a methanolic solution of the mononuclear benzobismidazole complex, in N₂ atmosphere. After purification, two main fractions showing very similar spectral profiles were collected. In fact, the IL transitions centered on the bipyridine and benzobisimidazole ligands, as well as the MLCT bands corresponding to both ruthenium complexes in the binuclear complex, were quite similar, as shown in figure 32.

Figure 32. UV-vis spectra of the two main fractions collected during the final column chromatography for separation/purification of the binuclear [$\{Ru(bpy)_2\}(dpimH_2)\{Ru(phtpy)Cl\}\}(ClO_4)_3$ complex.

Since, the geometry of the mononuclear $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)](\text{ClO}_4)_2$ complex allow the formation of two geometric isomers depending on the relative positions of the chloro ligands in the structure of the binuclear complex. In fact, the formation of two isomers (main fractions), the out- $[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{3+}$ and in- $[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{3+}$ isomers is expected. The optimized structures and calculated energy by DFT (B3LYP) of both isomers are shown in figure 33. Note that there is only a small energy difference of 8.8 kcal/mol between the isomers A and B indicating that there is no thermodynamic reason indicating the preferential formation of one of them, such that both can be produced in the reaction.

Figure 33. Geometric isomers of the binuclear $[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{3+}$ complex.

The ESI-MS spectra of these two main fractions are shown in figures 34 and 35. Both fractions exhibit two main peaks corresponding to doubly and triply positively charged species with m/z 585 ($\Delta m/z = 0.5$) and m/z 390 ($\Delta m/z = 0.3$), assigned respectively to the monoprotonated species $[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH})\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{2+}$ and the diprotonated $[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{3+}$ complex. Similarly to the mononuclear complex, the MS peaks of these dinuclear species showed the typical isotopomeric pattern correspondent to species containing two ruthenium ions, each of one with seven stable isotopes (^{104}Ru (18.7%), ^{102}Ru (31.6%), ^{101}Ru (17.0%), ^{100}Ru (12.6%), ^{99}Ru (12.7%), ^{98}Ru (1.88%), and ^{96}Ru (5.52%)).

Figure 34. ESI-MS spectrum correspondent to one of the geometric isomers (fraction 1a) of the $[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{3+}$ complex.

Figure 35. ESI-MS spectrum correspondent to another geometric isomer (fraction 2a) of the $[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{3+}$ complex.

The mass spectra of the fractions 1a and 2a were consistent with binuclear complexes and showed that both species have analogous molecular ions and fragmentation pattern, confirming that are isomers generated in the reaction. However, only some subtle differences observed in the UV-vis spectra could be used to identify each species until now. Accordingly, ^1H -NMR spectroscopy was used to elucidate their structure and allow a more precise description of each isomer.

As expected, the low symmetry of the binuclear complex generated a plethora of signals in the ^1H -NMR spectrum, and the one corresponding to “isomer B” fraction is shown in figure 36. At first, the J-coupling of the signals was analyzed to choose a reference to calculate the number of protons in the spectrum. Since the nature of the multiplets in the 8.20 to 7.20 ppm range don't allow such analysis, the proton at 8.69 ppm displays the higher $J = 8.2$ Hz value due to the strong coupling with protons in ortho and meta positions, that could be related with the proton Ha' from the phenyl substituent in the phtpy ligand whose integral is equivalent to two protons.

From the integration of Ha peak, the number of protons determined from the spectrum was 41. The imidazole -NH protons were not taken into account, even considering that the coordination of a second ruthenium ion would increase their basicity decreasing the rate of deuterium exchange with the protic deuterated solvent (MeOD). From the values of J-coupling in the 8.0 to 8.2 Hz, it is also possible to differentiate the eight Hd protons of the dpimH₂ ligand pyridyl moieties. Furthermore, although the region associated with the remaining protons is quite complex, it was possible to assign the protons at stronger field between 7.12 to 6.92 ppm with the Hb protons from the bipyridine ligands, since the chemical shift is pretty similar to those of the mononuclear complex (Fig. 31).

A detailed analysis of the ^1H -NMR spectrum allowed us to identify the presence of a second species in small amounts, in about 16 times lower concentration than the main compound. As shown in figure 18, the chloride ligand in the out- isomer can deshield the pyridine alpha proton as consequence of the diamagnetic anisotropy effect generated by that anionic ligand, yielding a doublet shifted to lower fields with respect to the in-complex. The signal at 10.12 ppm ($J = 5.2$ Hz) observed in the ^1H -NMR spectrum is consistent with the previous description, and allowed us identifying this second compound as the out- $[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{3+}$ complex and the main compound to the in- $[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{3+}$ complex (isomer B).

Figure 36. Scheme of the structure and ^1H -RMN (500 MHz) spectrum of isomer B in- $[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{3+}$, in acetonitrile- d_3 . An expanded view in the 7.3 to 8.3 ppm is also shown.

4.5. Electronic Spectroscopy and Electrochemistry

4.5.1. Mononuclear complex $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)](\text{ClO}_4)_2$

The electrochemical behavior of the $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)]$ complex was studied by cyclic voltammetry in MECN using a glassy carbon electrode. Figure 37 show a series of cyclic voltammograms in different potential windows to analyze the dependence of each wave with others and better evaluate their reversible/irreversible character. The CVs were registered during two or three scans to observe the displacement and increase of current associated to some redox processes after each cycle, to determine its nature.

In this way, the first scan (solid line) in figure 37a recorded from 1.6 V to -1.7 V initially showed a reversible pair of waves at $E_{1/2}=1.23$ V associated with the Ru(III/II) process in the mononuclear complex. In the cathodic region, from 0 to -1.7 V, the first cathodic wave was associated with the evolution of hydrogen by the reduction of the dpimH₂ ligand coupled with the reduction of H⁺. This was slightly shifted from -0.50 V

in the free ligand to -0.59 V in the ruthenium complex, since the acidity of the -NH moieties decrease due to the π -backbonding interaction with the coordinated Ru(II) ion. A similar shift was observed for the irreversible peak related with the reduction of dpimH⁻ to dpimH²⁻ species at -1.06 V in the free ligand, and at -1.09 V in the ruthenium complex. Finally, two pairs of reversible waves associated with the reduction of the bipyridine ligand to its radical anion bpy^{•-} were observed respectively at $E_{1/2}$ = -1.25 V and -1.51 V.

Figure 37. Cyclic voltammograms of the mononuclear $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)](\text{ClO}_4)_2$ complex ($1 \text{ mmol} \cdot \text{dm}^{-3}$) in different potential windows, at 100 mV/s in MeOH. The solid (—) dash (----) and dot (····) line correspond to the first, second and third successive scans respectively.

The second scan (dashed line, Fig. 37a) showed an irreversible oxidation peak at 0.89 V followed by the reversible wave of the $\text{Ru}^{2+}/\text{Ru}^{3+}$ redox pair ($E_{1/2}=1.23 \text{ V}$). To know the nature of these new peak, the electrochemical behavior of the $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)](\text{ClO}_4)_2$ complex was evaluated in different potential windows. Thus, in figure 37b is presented the first range tested, which cover the anodic region between 0.4 V and 1.6 V . It is observed that after ruthenium oxidation at 1.30 V (solid line) a new anodic wave emerges at 1.44 V , this pair of waves can be related with the oxidation of

the dpimH₂ ligand, that in relation to the free ligand (0.90 V) appear at higher potentials. The disappearance of the anodic wave at 0.89 V after three scans suggests that it is independent of the ruthenium or ligand oxidation processes, but depends on reduction processes occurring in the ligands. Accordingly, the potential window was expanded to the cathodic region.

In figure 37c is shown the CV recorded over a potential range from -0.90 V to 1.4 V to cover the first irreversible reduction of the dpimH₂ ligand and the oxidation processes of the complex. The voltammogram registered in this condition displayed again the anodic wave at 0.89 V after the first scan, whose intensity increased after each scan indicating that the reduced species is generated during the reduction process at -0.59 V. Analysis of these result suggest that the deprotonated dpimH₂ ligand can be more easily oxidized or the Ru²⁺/Ru³⁺ can be shifted to more negative potentials after reduction of H⁺ as consequence of its much stronger electron donor character. It seems that the diffusion rate of the deprotonated species, allows the electrochemical detection of both protonate and deprotonated complex on the electrode surface. Confirmation of this conclusion was obtained by limiting the potential range from -0.9 V to 1.0 V, as displayed in figure 37d. Note that, the process at 0.89 V appears as a reversible process after three scans allowing the assignment of this wave to a redox process involving the ruthenium center, i.e. to a Ru(III/II) process of the complex with deprotonated dpimH₂ ligand.

The spectroelectrochemical analysis of the [Ru(bpy)₂(dpimH₂)](ClO₄)₂ complex in the anodic region was carried out in acid media to avoid deprotonation of the -NH moieties after oxidation of the metal center from Ru(II) to Ru(III). In figure 38a it is possible to observe that the E_{1/2} of the couple Ru²⁺/Ru³⁺ is shifted 160 mV to more positive potentials and appear at 1.39 V in acid media (pH 2) as compared with the E_{1/2} in neutral conditions (Fig. 37b), probably due to the protonation of the free pyridine moiety. The spectroelectrochemical profile of the mononuclear complex in acid media in the 1.20 V - 1.45 V range (Fig. 38b) shows the decay of the metal-to ligand charge transfer (MLCT) band at 460 nm as Ru²⁺ is oxidized to Ru³⁺, concomitantly with the rise of a band at 850 nm. This was tentatively assigned to a LMCT band since the benzimidazole ligand exhibits good electron donor properties. On the other hand, the band at 290 nm related with the $\pi \rightarrow \pi^*$ transitions centered on the bipyridine ligand, showed a significant decay with the concomitant emergence of a band at 316 nm due to the oxidation of the ruthenium center. This spectroelectrochemical behavior is characteristic of bipyridyl ruthenium

complexes.^{53,54} The spectra depicted in gray lines show the spectral changes during the oxidation process before reaching the spectrum of the oxidized species (black line). The changes in intraligand bands profile is clearly shown, for example that involving the dpimH₂ ligand (360 nm).

Figure 38. Cyclic voltammogram of the mononuclear $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)](\text{ClO}_4)_2$ complex in acidified acetonitrile (a). Spectroelectrochemical behavior of the $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)](\text{ClO}_4)_2$ complex (b) during the oxidation in the 1.20 to 1.45 V range in acidified acetonitrile solution, and the reduction of the ruthenium center in neutral acetonitrile in the (c) -0.18 to -0.85 V range and (d) -0.85 to -1.44 V range.

Since the ligand reduction process are only available in organic solution, the spectroelectrochemical behavior of the complex in the region between 0 V to -1.6 V was studied in an acetonitrile solution. The UV-Vis spectra in figure 38c, shows the spectroelectrochemical profile of the complex in the potential range between -0.18 V to -0.85 V range where the reduction and deprotonation of the dpimH₂ ligand occurs. This is confirmed by the bathochromic shift of both the $\pi \rightarrow \pi^*$ transitions of dpimH₂ ligand (360 nm to 400 nm) and the MLCT band (460 nm to 500 nm) as explained by the smaller

energy gap between the HOMO and LUMO levels in the complex after deprotonation of the dpimH₂ ligand, as discussed above. As expected the behavior of the band centered in the dpimH₂ ligand, is consistent with that of the deprotonated species, as shown previously in figure 23. In the last range, from -0.85 V to -1.44 V (Fig. 38d), the second reduction of the dpimH₂ ligand and the first reduction of the bipyridine display takes place inducing significant changes in the intraligand bands. First, in the region of high energy, it is observed the decay of the band at 290 nm as expected for the formation of the 2',2-bpy^{•-} radical anion. In contrast, the rise of bands around 400, 492 and 532 nm is consequence of the reduction of the dpimH₂ ligand.

4.5.2. Binuclear in- $[\{Ru(bpy)_2\}(dpimH_2)\{Ru(phpty)Cl\}](ClO_4)_3$ complex

The cyclic and differential pulse voltammetry of the binuclear in- $[\{Ru(bpy)_2\}(dpimH_2)\{Ru(phpty)Cl\}](ClO_4)_3$ complex, using a glassy carbon electrode, is shown in figure 39a. The anodic region showed four waves that can be related with the oxidation process of the two metallic centers, which have different redox potentials since the binuclear complex is not symmetric. The voltammetric behavior is complicated by the possibility of oxidation of the dpimH₂ ligand and acid-base equilibrium coupled with those redox processes. In fact, those processes become more reversible when the potential window is limited to the 0.6 to 1.7 V range, and converge to two reversible processes characteristic of Ru(III/II) redox pairs when acidified with trifluoroacetic acid, thus inhibiting the dissociation of the N-H protons, as shown in figures 39b and 39c.

Thus, the first reversible peak at E_{ap} = 1.00 V related with the oxidation of Ru(II) to Ru(III) (figure 39c) can be assigned to the redox process centered on the $[RuCl(phpty)(dpimH_2)]^+$ moiety since the π -donor character of the -Cl ligand lower the redox potential as compared with the $[Ru(bpy)_2(dpimH_2)]^{2+}$ moiety. In contrast with the mononuclear species, the pyridine nitrogens of the binuclear complex are being used for coordination to the ruthenium sites and are not available for protonation even in acidic conditions. Accordingly, the pair of waves at E_{pa} = 1.41 V in figure 39c can be assigned to the Ru³⁺/Ru²⁺ redox couple involving the $[Ru(bpy)_2(dpimH_2)]^{2+}$ moiety whose potential is shifted anodically +100 mV in comparison with the analogous process in the mononuclear complex. This suggests that the oxidation of the first ruthenium site in the

binuclear complex increase the oxidation potential of the second ruthenium site as compared with the mononuclear complex.

Figure 39. Cyclic voltammograms (100 mV/s) and differential pulse voltammogram of a neutral acetonitrile solution of $\text{in-}[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}](\text{ClO}_4)_3$ complex from (a) -1.70 to 1.73 V and from (b) 0.53 to 1.73 V; and (c) after addition of trifluoroacetic acid in 0.53 to 1.73 V range. Electrode: glassy carbon, electrolyte: TBAClO_4 .

The spectroelectrochemical measurements in the anodic regions allow us to confirm the previous tentative assignments. In the potential range from 0.73 to 1.16 V the disappearance of the MLCT band at 547 nm (figure 40a), attributed to the oxidation of the $[\text{Ru}(\text{phtpy})\text{Cl}(\text{dpimH}_2)]$ moiety to the respective ruthenium(III) species, is observed. Concomitantly, the band at 328 nm related with the phtpy ligand decay together with the band at 360 nm centered on the dpimH₂ ligand, that also suffer a bathochromic shift. It is also notable the absorbance decrease of the MLCT band at 464 nm probably due to the disappearance of the MLCT band at 547 nm. At this point, it is important to mention that the bpy π - π^* transition remained almost unchanged confirming our assignment.

Figure 40. Spectroelectrochemical behavior of the in- $[\{\text{Ru}(\text{bpy})_2(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}](\text{ClO}_4)_3$ complex in acetonitrile solution acidified with trifluoroacetic acid, in the 0.73 to 1.38 V range.

As expected, the spectroelectrochemical behavior in the 1.23 to 1.48 V range (Fig. 40b) was consistent with the oxidation of the $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)]$ moiety of the binuclear complex to the ruthenium(III) species, as confirmed by the disappearance of the MLCT band at 464 nm and decay of the bpy intraligand band at 288 nm. This behavior is pretty similar to that observed in the mononuclear $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)](\text{ClO}_4)_2$ complex (Fig. 38b), in which the oxidation of the metal center lead to the disappearance of the MLCT band at 462 nm, followed by a significant decay of the bands at 362 nm and 291 nm attributed to the bis-bidentate dpimH₂ ligand and the bipyridine ligands respectively. Thus, this binuclear complex has an analogue of the photochemically active $[\text{Ru}(\text{bpy})_3]$ complex covalently bond to an analogue of a chloro complex that can be easily converted in the respective catalytically active aqua complex. Accordingly, the structure of our binuclear complex resemble of photosynthetic dyads, where the excited $[\text{Ru}(\text{bpy})_2\text{dpimH}_2]$ moiety may be able to oxidize the $[\text{Ru}(\text{phtpy})(\text{H}_2\text{O})(\text{dpimH}_2)]$ moiety to catalytically active high-valence states, whose lifetime is long enough to allow the oxidation of some substrates of interest such as water generating O₂. At the same time, the corresponding reducing equivalent would be used to reduce water generating H₂.

Back to figure 39a, the DPV showed more clearly the reduction waves of the Ru(III,III) binuclear species. Also, as in the mononuclear complex (Fig. 37a), the first irreversible peak at $E_{\text{pc}} = -0.55$ V is related with the formation of hydrogen gas coupled with the reduction of the dpimH₂ ligand. The spectroelectrochemical behavior in the -0.15 to -0.81 V range (Fig. 41a) showed the bathochromic shift of the dpimH₂ ligand band at 370 nm expected upon its deprotonation, as shown in figure 23, with minor changes on the bpy and phtpy intraligand π - π^* transitions respectively at 284 and 322 nm.

Figure 41. Spectroelectrochemical behavior of the in-[[Ru(bpy)₂](dpimH₂){Ru(phtpy)Cl}](ClO₄)₃ complex in acetonitrile solution, in the -0.15 to -1.70 V range.

Although in figure 39a the cathodic sweep below -0.81 V displayed several reduction processes with similar redox potentials, it was possible to distinguish some of them by spectroelectrochemistry. Thus, in the -0.81 to -1.30 V range (figure 41b) the decay of the bands at 288 and 324 nm can be related with the reduction of the bpy and phtpy ligands, respectively. The much subtle decay of the absorption at 393 nm and at 542 nm, concomitantly with the rise of a band at 694 nm probably is also associated with that process. The spectra collected from -1.30 to -1.50 V (Fig. 41c) showed an increase in the absorbance of the band centered in the bpy ligand, probably due to the formation of the radical anion species bpy^{•-} (288 nm) influencing the phtpy (328 nm) and dpimH₂ (402 nm) bands. Finally, in the -1.50 to -1.70 V range (Fig 41d), the band at 288 nm is observed decayed again and can be attributed to the reduction of the second bipyridine ligand. The high concentration of negative charge in the complex seems to increase the pK_a of the dpimH₂ bridging ligand which is protonated again, as suggested by the change in the absorption profile in the 352 and 428 nm, as shown previously in figure 23.

4.5.3. Redox-pH dependence of the $\text{in-}[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{3+}$ complex

The electrochemical behavior of the asymmetric binuclear $\text{in-}[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{3+}$ complex was investigated as a function of pH in the 2.0 to 9.0 range, in a $\text{CH}_3\text{CN}/\text{BR}$ Buffer 1/1 (v/v) solution.

Figure 42. Cyclic voltammograms in $\text{CH}_3\text{CN}/\text{buffer}$ (1/1, v/v) at $\text{pH} = 2.1, 3.1, 4.1, 6.1, 7.2, 8.1$ and 9.1 at a scan rate of 100 mV s^{-1} , on a glassy carbon electrode (a) and half-wave potential ($E_{1/2}$) as a function of the pH value (Pourbaix diagram) (b) of the asymmetric dinuclear complex $\text{in-}[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{3+}$.

As expected from the two different ruthenium complexes connected by dpimH_2 bridging ligand, two well resolved reversible redox processes can be observed in the voltammograms. In $\text{pH}=2.1$, the redox pairs observed at 1.1 and 0.84 V (figure 41) can be assigned to the Ru(III/II) process. Interestingly, both waves shift to more negative potentials as a function of pH, as expected for an electron transfer coupled with an acid-base reaction. In our case, the only acid-base site available are the imidazole $-\text{NH}$ groups of the bridging ligand. Thus, the oxidation of the ruthenium sites to Ru(III) should be associated with the deprotonation of the corresponding group due to the larger acidity of the oxidized moieties. Also, the deprotonation of the imidazole moieties in the binuclear complex increase the σ -donor ability of the bridging dpimH_2 ligand.

The CVs for the dyad displays two reversible one-electron $\text{Ru}^{3+}/\text{Ru}^{2+}$ pair of waves for all the range of pHs since it has two distinct types of ruthenium centers (chromophore and catalyst) in the dinuclear complex, making difficult the observation of any electronic coupling. However, it is possible to observe that the more positive one, assigned to the $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)]$ moiety, stops shifting at about $\text{pH}=6.1$ while the more

negative pair of waves continue shifting up to pH=9.1. This suggests that after the first deprotonation of the complex, probably of the -NH proton near that chromophore center around pH 6, the oxidation potential stay fixed for this center while the redox potential for the $\text{Ru}^{3+}/\text{Ru}^{2+}$ couple in the chloro complex remains decreasing as the pH increase. Until pH 6 the potential difference is ~280 mV but increased to 400 mV at pH 9. This indicates that this moiety has a higher pKa and can be even more easily oxidized by the chromophore center upon deprotonation at pHs above 6. In addition, this intramolecular electron transfer process will be more efficient if the deprotonation increase the electronic coupling between the two ruthenium centers of the asymmetric dinuclear in- $[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{3+}$ complex.

4.6. Unexpected behavior of the $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ complex

Considering the well established idea on the inertness and stability of ruthenium(III) terpyridine derivatives, the only possible hypothesis to explain the formation of the holeptic $[\text{Ru}(\text{phtpy})_2]$ complex in the reaction of $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ with bidentated ligands such as dpimH₂ as previously described, seems to be the presence of free phtpy ligand as complex **1** impurity, thus leading to the formation of $\text{Ru}(\text{phtpy})_2$ as major product. To test this hypothesis, we performed the characterization of the $[\text{RuCl}_3(\text{phtpy})]$ complex used as intermediate by CHN elemental analysis and ¹H-NMR to pursue for organic impurities, particularly free phtpy ligand.

The elemental analysis provided the following percentage of C= 45.00; H= 3.25 and N= 7.28, which reasonably matched the calculated elemental analysis for the dihydrated complex $[\text{RuCl}_3(\text{phtpy})]\cdot 2\text{H}_2\text{O}$, i.e., C= 45.62; H= 3.46; and N= 7.60.

The ¹H-RMN spectrum of $[\text{RuCl}_3(\text{phtpy})]$ (Fig. 43), recorded in DMSO-d₆, is characterized by the presence of broad and shifted signals due to the paramagnetic effect of S=1/2 high field Ru(III) ion. This indicates that the nuclear spin relaxation time of the protons close to the metal center (bonded to the terpyridine ring) was shortened and the corresponding NMR peaks broadened, while strongly shifted to high fields due to the effect of the electron spin on the local magnetic field. In contrast, the peaks corresponding to more distant phenyl ring protons appeared as sharper and more well resolved peaks facilitating the assignment of the Ha, Hb and Hc protons, as shown in Figure 43. Notice,

however, the presence of five signals in 9.0 to 7.5 ppm range, labeled with asterisks, assigned by comparison to the phtpy ligand bonded to a diamagnetic Ru(II) center. This species can be formed in situ since the EtOH used as solvent can act as a reducing agent, or the reduced species is formed during the synthesis of compound $[\text{RuCl}_3(\text{phtpy})]$. Furthermore, the signals labeled with dots indicates the presence of a small amount (3.8% with respect to the Ru(III) complex) of the $[\text{Ru}(\text{phtpy})_2]^{2+}$ complex as impurity, since it is formed as byproduct during the synthesis of the $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ complex.^{55,56}

Figure 43. ^1H -NMR spectrum (300 MHz) of the $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ complex in $\text{DMSO}-d_6$, and its reduced species $[\text{Ru}^{\text{II}}(\text{phtpy})\text{Cl}_3]$ labeled with asterisk, as well as the signals corresponding to the $[\text{Ru}(\text{phtpy})_2]^{2+}$ complex present as impurity (labeled with dots). The contrasting spectrum of free phtpy ligand in $\text{dmso}-d_6$ is shown in Figure 46.

Once proved the absence of free phtpy ligand as impurity in the complex, and after several attempts to avoid the formation of the bis(phenylterpyridine) complex as the main product, we accepted the possibly that the precursor complex $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ is in fact decomposing and releasing the phtpy ligand that is reacting with another $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ and forming the homoleptic $[\text{Ru}(\text{phtpy})_2]^{2+}$ complex and solvated RuCl_3 . In fact, there are few reports in the literature describing the formation of mixtures of hetero- and homoleptic ruthenium complexes when analogous terpyridine complex intermediates are reacted with different types of ligands.⁵² This suggests that the tridentated terpyridine ligand is dissociating from the $[\text{Ru}^{\text{III}}(\text{phtpy})\text{Cl}_3]$ complex leading to the formation of the homoleptic complex as major byproduct, a quite unusual hypothesis considering the well-known high stability of chelates and the inertness of ruthenium complexes, especially

Ru(III) complexes. In the attempt to get much stronger evidence to support this hypothesis, the supernatant of a suspension of $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ complex in methanol under stirring at room temperature, was monitored as a function of time by UV-Vis and by reflectance spectroscopy after TLC analysis (Fig. 44). Although an increase of absorbance at 490 nm was observed during the first 15 minutes, the formation of the homoleptic $[\text{Ru}(\text{phtpy})_2]$ complex was verified by TLC only after two hours, indicating that the phtpy ligand is effectively dissociating from the $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ complex before reacting with another $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ complex to generate the $[\text{Ru}(\text{phtpy})_2]$ complex.

Figure 44. Series of UV-vis spectra collected while monitoring a suspension of the $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ complex in MeOH (left). Note that almost no $[\text{Ru}(\text{phtpy})_2]$ complex MLCT band is observed at 490 nm at start (red line), and the UV-vis reflectance spectrum showed the bands corresponding to the $[\text{RuCl}_3(\text{phtpy})]$ precursor (dotted line). However, after 2h the MLCT band of the $[\text{Ru}(\text{phtpy})_2]$ complex is clearly seen in the solution (solid line). The spectrum of authentic homoleptic complex (dashed line) was included for comparison purpose.

Further evidence to reinforce our conclusion was obtained using ^1H -NMR spectroscopy (Fig. 45). A suspension of $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ in ethanol was stirred at 60°C , and dried in a flash evaporator after eight hours. The solid was dissolved in $\text{DMSO}-d_6$, its spectrum recorded, and compared with the spectrum of the free phtpy ligand, the $[\text{Ru}(\text{phtpy})_2]^{2+}$ complex and freshly prepared $[\text{RuCl}_3(\text{phtpy})]$ complex. Notice that this solution is mainly constituted by a mixture of oxidized and reduced $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ complexes, and a small amount (3.8%) of $[\text{Ru}^{\text{II}}(\text{phtpy})_2]^{2+}$ complex. After 8 hs at 60°C in ethanol, however, that amount of this species increased to 14.5% with the concomitant disappearance of the signals assigned to the reduced $[\text{Ru}^{\text{II}}\text{phtpyCl}_3]$ species, and the rise of weak signals indicating the presence of free phtpy ligand in solution, as indicated in light red brown.

Figure 45. ^1H -RMN (300 MHz) of the $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ complex in $\text{DMSO-}d_6$ in the 6 to 10.5 ppm range showing the peaks characteristic of the reduced $[\text{Ru}(\text{phtpy})\text{Cl}_3]^{2+}$ species, $[\text{Ru}(\text{phtpy})_2]^{2+}$ complex, free phtpy ligand and the mixture resultant from the heating of the mixture of oxidized and reduced $[\text{Ru}(\text{phtpy})\text{Cl}_3]$ complexes in EtOH during 8 hs.

This result clearly indicated that the oxidized species dissociates releasing free phtpy ligand, that reacts with $[\text{Ru}^{\text{II}}(\text{phtpy})\text{Cl}_3]$ complex generating the homoleptic $[\text{Ru}^{\text{II}}(\text{phtpy})_2]$ complex. In fact, this seems to be the driving force pushing the reaction towards the formation of $[\text{Ru}^{\text{II}}(\text{phtpy})_2]$ as the major byproduct. In fact, reactions of the bis-bidentated dpimbH₂ ligand with previously reduced $[\text{Ru}^{\text{II}}(\text{phtpy})\text{Cl}_3]$ complex lead to the successful preparation of the desired binuclear complexes reinforcing such hypothesis.

V. CONCLUDING REMARKS

A symmetric and an asymmetric dinuclear ruthenium complex was successfully prepared and characterized by spectroscopic and electrochemical methods. The asymmetric species is a molecular dyad where a photochemically active $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)]^{2+}$ moiety was connected to a $[\text{Ru}(\text{phtpy})\text{Cl}(\text{dpimH}_2)]^+$ moiety that can be easily converted to the respective aqua complex, the precursor of high valence oxoruthenium catalytic active species, through a benzo-bis-imidazole dpimH_2 bridging ligand. The symmetric species was prepared connecting two $[\text{Ru}(\text{phtpy})\text{Cl}(\text{dpimH}_2)]^+$ moieties through the dpimH_2 ligand in order to generate a prototype of a binuclear water oxidation center (WOC), in which a synergic interaction between both ruthenium sites are expected. All complexes were characterized by structural (CHN analysis, RMN, ESI-MS) and electrochemical (UV, CV, DPV, spectroelectrochemistry) techniques. The most prominent results of the work are summarized below.

The dpimH_2 ligand allows the formation of several geometric isomers depending on the relative position of the chloride ligand in each binuclear complex. Theoretical calculations showed that the isomers have similar energies, therefore the synthesis of the dinuclear WOC precursor can yield five geometric isomers whereas the dyad molecule yields two isomers. The presence of such geometric isomers was confirmed by column chromatography and mass spectrometry.

The acidic character of the $-\text{NH}$ protons in the bridging dpimH_2 ligand is affected by the back-bonding interaction with the coordinated $\text{Ru}(\text{II})$ center, as evidence by the cathodic shift of the respective $\text{Ru}(\text{III}/\text{II})$ redox potentials as a function of pH. In fact, the deprotonation of the imidazole $-\text{NH}$ imino moiety increase the donor character of the bridging dpimbH_2 ligand, that stabilizes the oxidized species and shifts the redox potentials. This demonstrates that it is possible to modulate the redox potentials of the dinuclear complexes simply by adjusting the pH of solution in order to shift the acid-base equilibrium involving that bridging ligand.

The $[\{\text{RuCl}(\text{phtpy})\}_2(\text{dpimH}_2)]^{2+}$ complex which includes two catalytic site precursors showed an increase of the electronic coupling between the two ruthenium centers upon deprotonation, as attested by the separation of the $\text{Ru}^{3+}/\text{Ru}^{2+}$ couple in two distinct reversible redox pairs. Similar behavior is expected for the asymmetric in-

$[\{\text{Ru}(\text{bpy})_2\}(\text{dpimH}_2)\{\text{Ru}(\text{phtpy})\text{Cl}\}]^{3+}$ dinuclear complex, in which the oxidation potential for both centers, the chromophore and catalyst, were shifted to less positive potentials as a function of pH. However, the electronic coupling cannot be easily evaluated in this case, but clearly the first pKa of the bridging ligand is about 6.2, and the potential difference between the centers increase for higher pHs. Although it is necessary to study more in depth the pH dependent behavior, these results are an additional evidence demonstrating the possibility of tuning the electrochemical and catalytic properties of those dinuclear complexes by controlling the acid-base reactions.

The preferential formation of the homoleptic $[\text{Ru}(\text{phtpy})_2]$ complex in the reaction media during the synthesis of the $[\{\text{RuCl}(\text{phtpy})\}_2(\text{dpimH}_2)]^{2+}$ complex was completely unexpected, and led to the formation of the desired ruthenium complexes in low yield. Also, the formation of that species caused a stoichiometric imbalance between the amount of dpimH_2 ligand and the $[\text{RuCl}_3(\text{phtpy})]$ complex, since involved the dissociation of the phtpy ligand and release of ruthenium ion species in the reaction medium. In the first case, such imbalance favored the formation of mono- and bi-nuclear complexes as the reaction proceeded. In the second case, the liberation of ruthenium ions and the dpimH_2 ligand favored the formation of polymeric species. This problem was solved by reducing the $[\text{Ru}^{\text{III}}\text{Cl}_3(\text{phtpy})]$ precursor to a Ru(II) species employing Zn(Hg) amalgam, that also seems to facilitate the dissociation of the chloro ligands and thus the formation of the desired binuclear complexes, with no significant formation of the bis-terpyridine complex. Since terpyridine-type complexes are mostly characterized by their stability, the dissociation of the phtpy ligand from $[\text{RuCl}_3(\text{phtpy})]$ to drive the formation of the complex $[\text{Ru}(\text{phtpy})_2]$ was completely unexpected. However, clear experimental evidences demonstrating the dissociation of the phtpy ligand from the trichloro complex were found, in order to strengthen that hypothesis to explain the formation of the cationic homoleptic ruthenium(II) complex as major product in the ligand substitution reactions involving the $[\text{RuCl}_3(\text{phtpy})]$ species.

VI. References

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APPENDICE

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Figure A1. COSY spectrum of the mononuclear $[\text{Ru}(\text{bpy})_2(\text{dpimH}_2)](\text{ClO}_4)_2$ complex in acetonitrile- d_3 .

INPUT GEOMETRY OPTIMIZATION

chk=cis_in_opt.chk

%NProcs=8

%mem=10GB

#P b3lyp/GEN

opt

Pseudo(read)

cis_in_opt

2 1

C -2.11710 4.55210 -1.83070

:

:

C H Cl N O

6-31g(d)

Ru 0

SDD

Ru 0

SDD

INPUT FREQUENCY CALCULATION

%oldchk=cis_in_opt.chk

%chk=cis_in_freq.chk

%NProcs=8

%mem=10GB

#p freq=noraman guess=read b3lyp/gen pseudo=read

cis_in_freq

2 1

C 1.15168 -4.37493 -0.09717

:

:

:

C H Cl N O

6-31g(d)

Ru 0

SDD

Ru 0

SDD

CURRICULUM VITAE

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Scientific Articles:

- 1) Paola A. Benavides, Tiago A. Matias and Koiti Araki, Unexpected lability of the $[\text{Ru}^{\text{III}}(\text{phtpy})\text{Cl}_3]$ complex, Dalton Transactions (submitted 18th August 2017).
- 2) Paola A. Benavides, Tiago A. Matias and Koiti Araki, Tunable binuclear ruthenium complex based water oxidation catalysts precursors (in preparation).

Academic Training

2005 Educational Institution San Vicente, Palmira – Colombia.

2014 Chemist graduate student, Universidad del Valle, Cali- Colombia.

2015 Young researcher, COLCIENCIAS – Universidad del Valle, Cali – Colombia.

2015/Present Master in chemical sciences - Chemistry Institute – Universidade de São Paulo, São Paulo – Brazil.

Research Experience

2014 Undergraduate Research Student, SIMERQO Polímeros, Chemistry Department, Universidad del Valle, Cali, Colombia. Project: Preparation of hidrazonic systems as precursors of polymers materials and supramolecular structures. Advisor: Manuel N. Chaur, Ph. D Area: Supramolecular chemistry and materials

2013 Summer Research Internship, LNNano, Centro Nacional de Pesquisa em Energia e Materiais (CNPEM), Brasil. Project: Preparation and characterization of multilayers based on Phthalocyanine, Advisor: Prof. Dr. Carlos Cesar Bof Bufon, Area: Materials science (with emphasis in Nanoscience and Nanotechnology).

2015 Young Researcher, SIMERQ Polimeros – GISIOMCA, Chemistry Department, Universidad del Valle, Cali, Colombia. Project: Preliminary studies for the formation of an adaptive hydrazonic polymeric material. Advisor: Manuel N Chaur, Ph. D. – Dr. Esperanza Galarza Area: Supramolecular chemistry and materials.

2015/Present Master Student, Laboratory of Supramolecular Chemistry and Nanotechnology LQSN, Chemistry Institute, Universidade de São Paulo, São Paulo-Brazil. Project: Synergistic Effects on Ruthenium Complexes Bridged by a Benzobisimidazole Ligand, Precursors of Water Oxidation Catalysts. Advisor. Prof. Dr. Koiti Araki. Area: Energy, Water and Environmental Sciences.

Teaching Activities

Monitor in the discipline. QFL 0140 - Química Inorgânica. Advisor: Prof. Dr. Vitor de Moraes Zamarion. Second Semester 2015.

Monitor in the discipline. QFL1231-2 - Química Inorgânica I: Química dos Elementos. Advisor: Prof. Dr. Koiti Araki. First Semester 2016.

Posters Presentations

- 24^a edição da Reunião Anual dos Usuários (RAU) do Laboratório Nacional de Luz Síncrotron. 2013

- III Simposio de Química Universidad del Valle. 2013.

- V Simposio de Química Universidad del Valle. 2016

- Paola A. Benavides, Tiago A. Matias, Koiti Araki, “Synergistic Effect of Dinuclear Ruthenium Complexes Bridged by a Bis-Imidazole Ligand for Water Oxidation”, 46th World Chemistry Congress – IUPAC 2017.