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# Complex formation equilibria of 2,2′-bipyridyl and 1, 10-phenanthroline with manganese(II) in methanol

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## Abstract

Water photolysis to molecular hydrogen and oxygen is one of the most promising chemical reactions for a sustainable hydrogen generation. The search for catalysts for this process is an important research area; some of the most suggested catalysts are manganese complexes. However, several studies propose the use of the complex: *tris*(bipyridine)ruthenium(II) chloride to be used as catalyst in artificial photosynthesis. In spite of this, the conferred properties by the 2,2′-bipyridyl ligand, in manganese or ruthenium complexes has not yet been discussed extensively.

In this work, in order to obtain more insight of the behavior of manganese(II) with several ligands such as 2,2′-bipyridyl or 1,10-phenanthroline, a spectrophotometric study of the speciation in methanol of these systems at 298 K, was performed. The formation constants obtained for the manganese(II)-2, 2′-bipyridyl system are: log $\beta_{110} = 7.81$ and log $\beta_{120} = 14.68$; for the manganese(II)-1,10-phenanthroline system are log $\beta_{110} = 6.94$ and log $\beta_{120} = 12.86$. These results were obtained by refining the experimental spectrophotometric data using the HypSpec software. In addition, a brief discussion of the comparison of the calculated individual electronic spectra of the complexes reported in this work with the spectrum of the *tris*(bipyridine)ruthenium(II) chloride and the manganese-calcium oxygen-evolving complex of photosystem II is presented.

*Keywords:* Artificial photosynthesis; Equilibria; Manganese(II) complexes

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## 1. Introduction

One of the most important reactions in nature, is the process of water splitting in molecular oxygen and ions hydronium using light [1]. This represents one of the most promising and challenging ways to generate a photochemical conversion and storing solar energy. It is also considered the starting point to a sustainable

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hydrogen generation [1–3]. Nowadays, energy systems based in hydrogen appears to be one of the most promising solutions in promoting a cleaner environment [4].

The photocatalytic water splitting occurs naturally during photosynthesis [2]. This process involves the absorption of light, water and $CO_2$ to produce food in the form of sugars, such as glucose, which plays a crucial role in for the growth and survival of plants. For this purpose, the plants employ two proteinic complexes localized in the thylakoid membranes of plants, algae and cyanobacteria: Photosystem I (PSI) and photosystem II (PSII) [2,5–7]. In PSI, the protons and electrons are involved in several redox reactions, by using the electrons transferred from photosystem II, through the complex Cytochrome-$b_6f$ and collaborate in the cycle of coenzyme $NADP^+$, which becomes NADPH, this provides the reducing power for $CO_2$ fixation, this is a complex process barely understood, which involves *The Calvin Cycle* [8]. On the other hand, the PSII contains the Oxygen-Evolving Complex (OEC), which is a cluster consisting in an oxo-connected structure that promotes the water splitting reaction [7]. In this catalytic site, the light contributes to splitting two water molecules to an oxygen molecule, 4 hydronium ions and 4 electrons [6]. Knowing the molecular structure of the OEC is a prerequisite for understanding and possible mimicking of the water splitting reaction and the metallic cluster involved. Numerous studies describe a possible mechanism promoted by the metallic core, however, the details of the true role of the structure of the OEC have not been fully revealed [9]. The cluster OEC consists of a tetra nuclear manganese arrangement, bonded to a calcium and chloride ions [6,10–12]. Different authors have been reported that in nature, this is the only system capable of catalyzing the oxidation of water [13,14].

The details of the catalytic mechanism of the water oxidation, remain controversial due to the uncertainties of the cluster structure, the sequence of changes in the oxidation states and the proton release pattern in the metal centers [2]. In the water splitting process, protons and electrons are released and several mechanisms have been proposed to explain the possible steps in this process. The mechanism widely diffused is the Kok cycle which is still debated in the scientific community [15,16]. Nevertheless, some other mechanisms have been proposed, such as Butterfly/double pivot, 2+2 and the nucleophilic attack of water/hydroxide to an electrophilic Mn=O bond. However, there is still no consensus about a true reaction pathway [15].

Molecular hydrogen in pure form is not available on Earth; however, methods for their production have been reported before. Among the different technologies for hydrogen production, natural or artificial oxygenic photosynthesis, have a great potential to produce hydrogen. Both of them use clean and cheap sources: water and solar energy [17]. Nevertheless, the sustainable molecular hydrogen production through direct conversion of solar energy into chemical energy, represent a great challenge [17]. The inspired process in natural photosynthesis, which uses solar energy to promote the chemical conversion of water and/or carbon dioxide to generate fuel, is known as artificial photosynthesis [18,19]. Usually, employs compounds that works as photosensitizers and collect solar energy. Also, it involves obtaining synthetic models to generate the catalytic activity for the hydrogen generation from the splitting water reaction [17].

The synthesis of metal clusters as structural models of the OEC and the development of artificial photosynthesis has a great field of potential application. Several metal complexes have been investigated for its use in artificial photosynthesis [20]. One of the most important complexes studied with potential water oxidation is the *tris*-(2,2′-bipyridyl) ruthenium (III) or $[Ru(bpy)_3]^{3+}$ [19–21]. Some other catalysts have been reported with the capacity for water oxidation. However, they are based on high priced metallic salts or with teratogenic effects [22]. Although, there are only a few reports about manganese complexes capable of catalyzing the oxidation of water [2,19], manganese is a promising metal to be used in artificial photosynthesis because of its low cost, owing to the fact that it is environmentally friendly and is naturally contained in the oxygenic cluster of photosynthesis II [2,20].

Some spectral analogies can be observed in both, natural and artificial systems for photosynthesis. In natural systems, although several transition states are present in the oxygen-evolving complex for example, in the spinach chloroplast [23], the spectral analogies between transition states usually present an absorption band at 310 nm. This signal is usually observed and is probably related to the change in the oxidation states of manganese and the geometry of each manganese site [8]. This characteristic may represent an important guide to mimic the electronic structure of the oxygen-evolving complex using coordination compounds. On the other hand, the compound $[Ru(bpy)_3]^{3+}$ and other similar ruthenium compounds have been widely studied. Several reports suggest that this compound could be used as a photoredox catalyst in water oxidation [2,21,24]. Usually presents the highest absorption band at approximately 285 nm [25].

In this work, the formation constants of the complexes generated with manganese(II), 2,2′-bipyridine