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Short communication

Spectrophotometric determination of the formation constants of calcium(II) complexes with 2,2’-bipyridyl and 1,10-phenanthroline in acetonitrile

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Abstract

The oxygen-evolving complex (OEC), which consists of a calcium-manganese cluster, is the reaction center of the Photosystem II. At this catalytic site, the water-splitting reaction in dioxygen and hydronium ions occurs. In order to partially reproduce the water splitting process, several studies have reported the synthesis of functional model complexes. Nevertheless, there is a small amount of reports, concerning the spectral behavior of calcium complexes or the calcium role in the cluster. In this work, in order to explore the absorption spectrum of calcium species in acetonitrile, an equilibrium study of the calcium complexes with 2,2’-bipyridyl or 1,10-phenanthroline, was carried out. The formation constants and the calculated electronic spectrum of each complex was obtained by a modified method of continuous variations consisting in a correlation of the experimental spectrophotometric data with the HypSpec software. The values of the formation constants for the calcium(II) complexes with 2,2’-bipyridyl and 1,10-phenanthroline, are $\text{Log } \beta_{110} = 4.39 \pm 0.02$ and $\text{Log } \beta_{110} = 5.94 \pm 0.05$, respectively.

Keywords: Artificial photosynthesis; Calcium complexes; Equilibrium

1. Introduction

The most important reaction for living beings is possibly the reaction of photosynthesis [1,2]. In this process, CO_2 is used to produce carbohydrates, which serve as an energy source for several organisms [3]. The reaction of photosynthesis takes place at the structures named Photosystem I and Photosystem II [4,5] in plants, algae and cyanobacteria [1,2,6,7]. In Photosystem II we find the oxygen-evolving complex which consists of a tetranuclear cluster of manganese, calcium, and chloride ions [8]. This structure represents the active site of the splitting water reaction [9,10]. In this process, sunlight is used to split water into dioxygen and hydronium ions [1,2]. Several research groups describe in detail the structure of the oxygen-evolving complex of the thermophilic cyanobacterium: *Thermosynechococcus vulcanus*, evidencing that the cluster calcium-manganese may have the empirical formula: $CaMn_4O_5(H_2O)_4$ [11].

There is growing interest in the production of molecular hydrogen as a form of environmentally-friendly renewable technology [12]. Inspired by the process of photosynthesis, in recent years, several research groups have proposed an innovative approach to dihydrogen production; this technology is known as artificial photosynthesis [7,13]. Currently, this approximation represents one of the most promising ways to generate dihydrogen and promote the storing of solar energy [14]. Several research groups have focused on the synthesis of a metal complex as a reaction center for charge separation and as

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a catalyst in oxidation-reduction reactions [15], or species for absorbing light [14]. The mechanism of oxidation of water by photosystem II is not fully understood [2,16–18], some mechanistic pathways from theoretical investigations and inorganic modeling of the complex, have been proposed [9]. On the other hand, the calcium ion is involved in a wide range of different activities in biological systems [15], several authors have proposed its possible roles in the oxygen-evolving complex [19]. However, its role remains controversial, it is believed to have functional and structural purposes [20]. Some of the possible aspects in which calcium could be involved in the water splitting reaction: is the dehydrogenation of the Mn-OH_xO cluster, electronic stabilization of oxo-species, regulate high oxidation states and possibly intervenes in the access of water molecules to the active site of the cluster [21]. Finally, it is possible that calcium ions might help to stabilize the oxidation states of manganese at high temperatures [22]. Nevertheless, as far as we know, the use of calcium complexes has not been considered in artificial photosystems.

The production of green hydrogen from sustainable energy sources is an actively developing technology [23]. Energy production through the direct conversion of solar energy into chemical energy remains a challenge today [3]. Several factors have limited the study of the coordination chemistry of calcium complexes, such as its solubility in several solvents. Information regarding the structures and binding sites of calcium complexes are difficult to obtain using techniques other than X-ray crystallography [24]. In this work, we report the formation constants and their speciation, of the complexes generated with Calcium(II), 2,2'-bipyridyl (Bpy) or 1,10-phenanthroline(Phen) in acetonitrile solution. The purpose of the present work was to obtain and explore the individual electronic spectrum of the complexes of Calcium(II) with 2,2'-bipyridyl (Bpy) and 1,10-phenanthroline(Phen).

2. Experimental

2.1. General

In the determination of the formation constants, the acetonitrile (CH_3CN) HPLC grade, is used as a solvent (Tecsiquim, Mexico), Calcium nitrate tetrahydrate, $Ca(NO_3)_2{\cdot}4H_2O$, 2,2′-Bipyridyl $(C_5H_4N)_2$ and 1,10-Phenanthroline $(C_{12}H_8N_2)$ (Sigma-Aldrich) were of analytical grade and used without further purification. All spectral measurements were made on a Cary 50 UV–Vis Spectroscopy System, at 298 K (RT) using a quartz cell with 1 cm of path length and 3 mL volume. For all the experiments, the observed spectral region was from 200 nm to 350 nm. For the determination of formation constants, the spectrophotometric data were fitted with the program HypSpec [25]. Distribution diagrams of species were calculated using the software Hyperquad Simulation and Speciation (HySS) [26].

2.2. Calcium(II)-2,2'-bipyridyl equilibrium studies

Experiments were performed using two different stock solutions of 2,2'-bipyridyl (358 and 250.8 µM). $Ca(NO_3)_2{\cdot}4H_2O$ was used to prepare Calcium stock solutions (237.2 and 166.1 µM). In each experiment, the final concentration of Calcium(II) was set constant at 23.72 µM and 16.6 µM, in where the 2,2'-bipyridyl concentrations were varied from 3.58 µM to 53.76 µM and 2.51 µM to 40.1 µM, respectively. A total of 29 spectra were used for the refinement in the HypSpec software, using the modified continuous variations method [27].

2.3. Calcium(II)-1,10-phenanthroline equilibrium studies

Experiments were performed using two different stock solutions of 1,10-phenanthroline (280 and 120 µM). $Ca(NO_3)_2{\cdot}4H_2O$ was used to prepare ionic calcium stock solutions (237.4 µM and 101.7 µM). In both experiments, the final Calcium(II) concentration was set constant at 23.72 and 10.17 µM and the 1,10-phenanthroline concentrations were varied from 2.8 to 56.0 µM and from 1.2 µM to 24.0 µM, respectively. A total of 38 spectra were used for the refinement in the HypSpec software, as described above.

3. Results and discussion

The calcium complexes reported here, are insoluble in several solvents, such as water, methanol or ethanol. Considering the low donor number or donicity of solvents [28,29], acetonitrile was used instead of the solvents above mentioned. The low donor number of acetonitrile (14.1), against the methanol (19.0) or ethanol (18.5), allows the preparation of solutions at very low concentration, avoiding precipitation of the complexes [28]. Also, ionic strength was not used because it can cause an early precipitation of the complexes; this consideration decreases the ionic solvation sphere and interferes with the stability of the complexes. Finally, the formation constants in this study cannot be regarded as true equilibrium constants and can only be used when they are compared with similar systems using the same method and solvent.

3.1. Formation constants of the calcium(II)-2,2'-bipyridyl and calcium(II)-1,10-phenanthroline complexes

The equilibrium constants for the complexes: Calcium(II)-2,2'-bipyridyl and Calcium(II)-1,10-phenanthroline, have been reported under several conditions and methods. A brief review of these systems is presented in Table 1. Nevertheless, as far as we know, the formation constants of the calcium(II)-2,2'-bipyridyl complexes, have not been reported before in the absence of ionic strength and acetonitrile as solvent. Also, to our knowledge, the electronic spectrum of the calcium complexes with 2,2'-bipyridyl or -1,10-phenanthroline has not been calculated in any other work.

In solution, the formation constants of the system of Calcium(II)-2,2'-bipyridyl has been reported in several solvents and methods: using spectrophotometry as a titration method, ethanol (95%) as solvent, murexide as an indicator, and tetraethylammonium perchlorate (TEAP) 0.05 M as ionic strength [31]; using a titration fluorometric method in acetone and ethanol as solvents, in the absence of ionic strength [32]; using a glass electrode, KCl as ionic strength at 0.20 M [33];