Solution Equilibria Formation of Manganese(II) Complexes with Ethylenediamine, 1,3-Propanediamine and 1,4-Butanediamine in Methanol

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Abstract: Manganese is an abundant element that plays critical roles and is at the reaction center of several enzymes. In order to promote an understanding of the behavior of manganese(II) ion with several aliphatic ligands, in this work, the stability and spectral behavior of the complexes with manganese(II) and ethylenediamine, 1,3-propanediamine, or 1,4-butanediamine were explored. A spectrophotometric study of its speciation in methanol was performed at 293 K. The formation constants obtained for these systems were: manganese(II)-ethylenediamine log $\beta_{110} = 3.98$ and log $\beta_{120} = 7.51$; for the manganese(II)-1,3-propanediamine log $\beta_{110} = 5.08$ and log $\beta_{120} = 8.66$; and for the manganese(II)-1,4-butanediamine log $\beta_{110} = 4.36$ and log $\beta_{120} = 8.46$. These results were obtained by fitting the experimental spectrophotometric data using the HypSpec software. The complexes reported in this study show a spectral pattern that could be related to a chelate effect in which the molar absorbance is not directly related to the increase in the carbon chain of the ligands.

Keywords: manganese(II) complexes; equilibria; formation constants

1. Introduction

Manganese(II) is a highly abundant and stable metal ion [1], which is considered a hard Lewis acid [2]. In nature, manganese plays critical roles in several proteins [1]. It is usually at the reaction center of several enzymes, such as superoxide dismutase, pyruvate carboxylase [3], and at the oxygen-evolving complex (OEC) in the photosynthesis II system [4], which is the catalytic site responsible for the water oxidation reaction to molecular oxygen [5–8]. Manganese is reported as the unique affordable and sustainable element, capable of catalyzing water splitting in nature systems [9] and is therefore considered an excellent candidate for its use in an artificial photosynthesis system [10]. In order to understand the electronic spectra of manganese complexes and promote an approach to mimic the spectrum of the oxygen-evolving complex [11], in recent years, several manganese complexes have been synthesized as models [12–15]. Some of these studies involved the use of simple ligands to generate an artificial OEC cluster [16]. Most of the manganese(II) complexes reported the use of a nitrogen-donor aromatic ligand, such as pyrazines or bipyridines [17]; a few studies also used aliphatic diamines as ligands [18,19]. In this work, with the purpose to explore the electronic spectra of manganese(II) complexes and compare them with the electronic spectra of OEC, an equilibrium study is conducted involving the formation constants, speciation and the calculated individual electronic spectrum of the complexes with manganese(II) and diamine ligands: ethylenediamine (en), 1,3-propanediamine (pn) and 1,4-butanediamine (bn) in a methanol solution. Additionally, the distinct effects of increasing the carbon atoms number of these ligands are discussed. To our knowledge, there are no reported studies of the Mn(II) with pn and bn. In contrast, manganese–ethylenediamine systems have been reported previously in various
solvent mixtures. Nevertheless, their equilibrium constants have not been reported in pure methanol.

2. Results and Discussion

In order to compare the results obtained in this study to our previous investigations [20,21], in all equilibrium measurements, ionic strength was avoided. This allows the use of a wide concentration range of ligands (either ethylenediamine, 1,3-propanediamine or 1,4-butanediamine). The formation constants obtained should not be considered true stability constants and must only be compared with systems measured under similar conditions.

2.1. Formation Constants of Manganese(II) Systems with Ethylenediamine, 1,3-Propanediamine or 1,4-Butanediamine

The electronic spectra collected for the systems of manganese(II) with ethylenediamine, 1,3-propanediamine and 1,4-butanediamine in methanol are shown in Figures 1–3, respectively. For these systems, as the ligand concentration increases, the hyperchromic effect begins to appear in the range of 240 to 260 nm. The formation constants $\beta_{jkl}$ were obtained by processing the spectra of two experiments at two different concentrations of manganese(II), and each experiment was performed using different ranges of concentrations of ligands (either ethylenediamine, 1,3-propanediamine or 1,4-butanediamine). The values obtained correspond to the equilibria between $\text{Mn}^{2+}$ and each ligand. The method generates a correlation between the spectrum obtained, the concentration of manganese(II), the ligand used and the proposal of the possible colored species.

In these systems, only two colored species and $\text{Mn}^{2+}$ were found. The formation constants were achieved using the following model (where $L$ is en, pn or bn):

\[
\text{Mn}^{2+} + L \rightleftharpoons [\text{Mn}(L)]^{2+} \log \beta_{110} \tag{1}
\]

\[
\text{Mn}^{2+} + 2L \rightleftharpoons [\text{Mn}(L)_2]^{2+} \log \beta_{120} \tag{2}
\]

Figure 1. Absorption spectra of manganese(II)–ethylenediamine system in methanol solution. For spectra 1 to 17, $[\text{Mn}^{2+}] = 0.16$ mM and ethylenediamine concentration (mM): (1) 0.054; (2) 0.072; (3) 0.09; (4) 0.108; (5) 0.126; (6) 0.144; (7) 0.16; (8) 0.18; (9) 0.198; (10) 0.216; (11) 0.234; (12) 0.252; (13) 0.27; (14) 0.288; (15) 0.306; (16) 0.324; (17) 0.342. For spectra 18 to 37, $[\text{Mn}^{2+}] = 0.3$ mM and ethylenediamine concentration (mM): (18) 0.03; (19) 0.06; (20) 0.09; (21) 0.12; (22) 0.15; (23) 0.18; (24) 0.21; (25) 0.24; (26) 0.27; (27) 0.3; (28) 0.33; (29) 0.36; (30) 0.39; (31) 0.42; (32) 0.45; (33) 0.48; (34) 0.51; (35) 0.54; (36) 0.57; (37) 0.60.
Figure 2. Absorption spectra of manganese(II)-1,3-diaminopropane complexes in methanol solution. For spectra 1 to 20, [Mn(II)] = 0.144 mM and 1,3-diaminopropane concentration (mM): (1) 0.0144; (2) 0.0288; (3) 0.0432; (4) 0.0576; (5) 0.072; (6) 0.0864; (7) 0.1008; (8) 0.1152; (9) 0.1296; (10) 0.144; (11) 0.1584; (12) 0.1728; (13) 0.1872; (14) 0.2016; (15) 0.216; (16) 0.2304; (17) 0.2448; (18) 0.2592; (19) 0.2736; (20) 0.288. For spectra 20 to 40, [Mn(II)] = 0.288 mM and 1,3-propanediamine concentration (mM): (21) 0.0288; (22) 0.0576; (23) 0.0864; (24) 0.1152; (25) 0.144; (26) 0.1728; (27) 0.2016; (28) 0.2304; (29) 0.2592; (30) 0.288; (31) 0.3168; (32) 0.3456; (33) 0.3744; (34) 0.4032; (35) 0.432; (36) 0.4608; (37) 0.4896; (38) 0.5184; (39) 0.5472; (40) 0.576.

Ethylenediamine, 1,3-propanediamine and 1,4-butanediamine are bidentate ligands [22], which usually generate -mono or -bis complexes [23]. Table 1 indicates the logarithmic values of the formation constants and a summary of the experimental parameters of these systems using the format by Tuck [24]. Therein, it can be observed that the formation constants of manganese(II) complexes with ethylenediamine change from 3.98 to 7.51 for -mono and -bis complexes, respectively. On the other hand, the formation constants of man-
ganese(II) complexes with 1,3-propanediamine change from 5.08 to 8.66 for -mono and -bis complexes, respectively. Finally, for the manganese(II) complexes with 1,4-butanediamine, they change from 4.36 to 8.46 for -mono and -bis complexes, respectively. Although aliphatic diamines have not been extensively explored as nitrogen-donor ligands in manganese(II) complexes, it has been reported that they might show a high conformational flexibility [23] and possibly induce a sigma donation to the metal center [25].

Table 1. Summary of experimental parameters for systems with manganese(II) and ethylenediamine, 1,3-propanediamine or 1,4-butanediamine, in methanol.

| Solution composition | Ionic strength, electrolyte | pH range | Experimental method | Temperature | Total number of data points | Method of calculation | Species | Equilibrium | Log $\beta$ | $\sigma$ | [Mn(en)]$^2^+$ | [Mn(en)$_2$]$^{2^+}$ | [Mn(pn)]$^2^+$ | [Mn(pn)$_2$]$^{2^+}$ | [Mn(bn)]$^2^+$ | [Mn(bn)$_2$]$^{2^+}$ |
|----------------------|-----------------------------|--------|---------------------|-------------|-----------------------------|----------------------|---------|-----------|-----------|--------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| [T$_L$] range from 0.054 to 0.342 and 0.030 to 0.600 mM | Not used | Not used | Spectrophotometric titration | 20 °C | Mn complexation: 37 solution spectra | HysSpec | Mn$^{2^+}$ + en $\rightleftharpoons$ [Mn(en)]$^{2^+}$ | $\log \beta_{110} = 3.98 \pm 0.029$ | 0.003 |
| [T$_M$] constant at 0.16 and 0.3 mM | | | | | | | Mn$^{2^+}$ + 2 en $\rightleftharpoons$ [Mn(en)$_2$]$^{2^+}$ | $\log \beta_{120} = 7.51 \pm 0.021$ | |
| Solution composition | Ionic strength, electrolyte | pH range | Experimental method | Temperature | Total number of data points | Method of calculation | Species | Equilibrium | Log $\beta$ | $\sigma$ | [Mn(pn)]$^2^+$ | [Mn(pn)$_2$]$^{2^+}$ | [Mn(bn)]$^2^+$ | [Mn(bn)$_2$]$^{2^+}$ |
| [T$_L$] range from 0.014 to 0.288 and 0.028 to 0.576 mM | Not used | Not used | Spectrophotometric titration | 20 °C | Mn complexation: 40 solution spectra | HysSpec | Mn$^{2^+}$ + pn $\rightleftharpoons$ [Mn(pn)]$^{2^+}$ | $\log \beta_{110} = 5.08 \pm 0.033$ | 0.004 |
| [T$_M$] constant at 0.144 and 0.288 mM | | | | | | | Mn$^{2^+}$ + 2 pn $\rightleftharpoons$ [Mn(pn)$_2$]$^{2^+}$ | $\log \beta_{120} = 8.66 \pm 0.023$ | |
| Solution composition | Ionic strength, electrolyte | pH range | Experimental method | Temperature | Total number of data points | Method of calculation | Species | Equilibrium | Log $\beta$ | $\sigma$ | [Mn(bn)]$^2^+$ | [Mn(bn)$_2$]$^{2^+}$ | [Mn(bn)]$^2^+$ | [Mn(bn)$_2$]$^{2^+}$ |
| [T$_L$] range from 0.016 to 0.320 and 0.032 to 0.576 mM | Not used | Not used | Spectrophotometric titration | 20 °C | Mn complexation: 38 solution spectra | HysSpec | Mn$^{2^+}$ + bn $\rightleftharpoons$ [Mn(bn)]$^{2^+}$ | $\log \beta_{110} = 4.36 \pm 0.044$ | 0.007 |
| [T$_M$] constant at 0.160 and 0.320 mM | | | | | | | Mn$^{2^+}$ + 2 bn $\rightleftharpoons$ [Mn(bn)$_2$]$^{2^+}$ | $\log \beta_{120} = 8.46 \pm 0.020$ | |

As far as we know, the formation constants for the manganese(II) systems with en, pn or bn in methanol without ionic strength and using a spectrophotometric method have not been reported. Nevertheless, there are a few studies of the manganese(II)-ethylenediamine system in solution using several methods and solvents. Table 2 offers a brief review of these systems. The calorimetric method (ionic strength of 0.05 N and buffer of NH$_4$Cl-NH$_3$) [26] uses glass electrode and a mixture of solvents of water/methanol, dioxane, acetonitrile or dimethylformamide (DMF) (with ionic strength of 0.1 M) [27] and dimethyl sulfoxide (DMSO) as solvent [28]. In order to compare the values of the formation constants obtained in this work with the values reported in Table 2, several differences should be taken into account, such as the method, solvent and experimental conditions. An important factor used in the measurements is the solvent donor number: in methanol (19), dioxane (14.8), acetonitrile (14.1), DMF (26.6) and DMSO (29,8), which represents the nucleophilic ability of solvents to accept or donate electron pairs [29]. It might influence the chelate effect in the complexes [30]. Nevertheless, the formation constant values for the
manganese(II)–ethylenediamine system obtained in this work are analogous to some of the studies shown in Table 2. A change of the solvent affects the binding properties of the ligand [31]. However, the equilibrium experiments in methanol have several advantages; the donor numbers of methanol (19) and water (18) are closer, and possibly, their solvation spheres are analogous [29].

Table 2. Stability constants of the complexes of manganese(II) with ethylenediamine under several conditions.

| Method     | Solvent          | Ionic Strength | T(K) | Logβ₁₁₀ | Logβ₁₂₀ | Logβ₁₃₀ | Ref.     |
|------------|------------------|----------------|------|---------|---------|---------|----------|
| Cal. Buffer NH₄Cl-NH₃ | 0.0510 N AgNO₃ | -              |      | 2.76    | 4.87    | 5.76    | [26]     |
| Glass Electrode | Methanol/Water (%) | 0.1 M KNO₃ | 298  | 2.85    | 4.75    | -       |          |
|            | 55               | 3.03           |      |                     |         |         |          |
|            | 60               | 3.07           |      |                     |         |         |          |
|            | 65               | 3.11           |      |                     |         |         |          |
|            | 70               | 3.15           |      |                     |         |         |          |
|            | 75               | 3.23           |      |                     |         |         |          |
|            | 80               | 3.26           |      |                     |         |         |          |
| Glass Electrode | Dioxane/Water (%) | 0.1 M NaClO₄ | 298  | 2.79    | 4.69    | -       | [28]     |
|            | 0                | 2.93           |      |                     |         |         |          |
|            | 20               | 3.16           |      |                     |         |         |          |
|            | 40               | 3.16           |      |                     |         |         |          |
|            | 50               | 3.33           |      |                     |         |         |          |
|            | 60               | 3.57           |      |                     |         |         |          |
|            | 70               | 3.90           |      |                     |         |         |          |
|            | 75               | 4.06           |      |                     |         |         |          |
|            | 80               | 4.27           |      |                     |         |         |          |
| Glass Electrode | Acetonitrile/Water (%) | 0.1 M of KNO₃ | 298  | 2.98    | -       | -       |          |
|            | 20               | 3.29           |      |                     |         |         |          |
|            | 40               | 3.44           |      |                     |         |         |          |
|            | 50               | 3.65           |      |                     |         |         |          |
|            | 60               | 3.90           |      |                     |         |         |          |
|            | 70               | 4.10           |      |                     |         |         |          |
|            | 75               | 4.40           |      |                     |         |         |          |
|            | 80               | 4.40           |      |                     |         |         |          |
| Glass Electrode | DMF*/Water (%) | 0.1 M of KClO₄ | 298  | 3.7     | 6.9     | 10.1    |          |
|            | 20               | 3.95           |      |                     |         |         |          |
|            | 40               | 3.14           |      |                     |         |         |          |
|            | 50               | 3.26           |      |                     |         |         |          |
|            | 60               | 3.40           |      |                     |         |         |          |
|            | 70               | 3.59           |      |                     |         |         |          |
|            | 75               | 3.71           |      |                     |         |         |          |
|            | 80               | 3.95           |      |                     |         |         |          |

*Cal. = calorimetry; DMF = N,N-dimethylformamide; DMSO = dimethyl sulfoxide.

The calculated electronic spectrum for manganese(II) complexes with ethylenediamine, 1,3-propanediamine or 1,4-butanediamine are shown in Figures 4–6, respectively. The manganese(II) complexes with ethylenediamine, 1,3-propanediamine or 1,4-butanediamine show a molar absorption between 220 to 260 nm, with a strong resemblance between them. In the study of metal complexes, the electronic spectrum can provide important information on the structure or nature of bonds in a complex. Nevertheless, specific signals with intense absorption are not clearly noted by considering this, in order to compare the electronic spectra of the species, 220 nm was selected as an arbitrary wavelength value. The molar extinction coefficients (ε) at 220 nm for the mono-complexes of Mn(II) with en, pn and bn are 10,900 L mol⁻¹ cm⁻¹, 10,300 L mol⁻¹ cm⁻¹ and 9634.3 L mol⁻¹ cm⁻¹, respectively. For the bis-complexes, they are 11,300 L mol⁻¹ cm⁻¹, 11,900 L mol⁻¹ cm⁻¹ and 11,653 L mol⁻¹ cm⁻¹, respectively. For mono-complexes, the order of molar absorbance
in this study is \( pn \approx bn > en \); for the bis-complexes, it is \( pn \approx en > bn \). The order of the formation constants for the mono-complexes is \( pn > en \approx bn \), and for the bis-complexes, it is \( pn \approx bn > en \). Due to the increase in the carbon chain in each ligand, an increase in the molar absorbance and stability should also be expected. The use of 1,4-butanediamine as a ligand allows us to theorize a decrease in the chelate effect due to its chain length. This behavior was reported before in copper complexes [23]. Considering that only the N-donor atom of each ligand could bond to manganese(II), in consequence, the mono or bis-species might present a decreased charge transfer and stability. On the other hand, while the formation constants are compared to other metals under similar conditions, such as Cu\(^{2+}\), the formation constants of the cupric complex with \( pn \) and \( bn \) [23] are much larger than those obtained in this study. This difference could be explained considering the proportion charge to the atomic radius. The relative stability of transition metal complexes corresponds to the Irving–Williams series, which indicates the increasing covalent interactions and electrostatic contributions in the metal–ligand bond [32].

Figure 4. Calculated electronic spectrum of the manganese(II)–ethylenediamine species in methanol: 
(1) Mn\(^{2+}\); (2) [Mn(en)]\(^{2+}\); (3) [Mn(en)\(_2\)]\(^{2+}\).

Figure 5. Calculated electronic spectrum of the Manganese(II)–1,3-propanediamine species in methanol: 
(1) Mn\(^{2+}\); (4) [Mn(pn)]\(^{2+}\); (5) [Mn(pn)\(_2\)]\(^{2+}\).
Figure 6. Calculated electronic spectrum of the manganese(II)–1,4-butanediamine species in methanol: (1) Mn$^{2+}$; (6) [Mn(bn)]$^{2+}$; (7) [Mn(bn)$_2$]$.^{2+}$.

Although several electronic transitions might occur in manganese(II) complexes, the absorption bands between 240 and 260 nm might correspond to ligand field transitions or d-d transitions [33]. At the range of 220 to 240 nm for manganese(II) complexes with en, pn or bn, the transition from the $\sigma$ orbitals to $e_g$ orbitals probably occurs [33,34]. It is important to mention that aliphatic ligands analogous to en, pn and bn are of the middle field and are therefore $\sigma$ donors only, with no orbitals of appropriate symmetry for $\pi$ bonding. The $\sigma$ interactions are usually between the $d_{z^2}$ orbital of manganese(II) and $p$ orbital of the ligand [34]. Of the opposite behavior, manganese(II) complexes with aromatic ligands have maximum absorbance to longer wavelengths [35], which are promoted by the intra-ligand absorption $\pi \rightarrow \pi^*$ [21,36,37] or $n \rightarrow \pi^*$ absorptions [21,38–40], which are not observed here. In the present study, the complexes show a maximum absorbance between the wavelengths of 240 to 260 nm. However, the spectrum of OEC reported by Lavergne [41] or Van Leeuwen [42] have a maximum absorbance at longer wavelengths (310–320 nm), while the molar absorbance of the OEC is about 6800 L mol$^{-1}$ cm$^{-1}$. The manganese(II) bis-complexes used in this study have a maximum absorbance closer to these values. The exploration and analysis of the spectra of manganese complexes using simple ligands can be an aid to understanding the electronic spectrum of OEC [43]. Analyzing the similarities between the complexes reported here with diamine simple ligands and the electronic signals of OEC can be an aid to gradually evolve an electronic model complex and reproduce the electronic spectra of OEC, which might contribute to its understanding.

2.2. Distribution Curves of the Manganese(II) with Ethylenediamine, 1,3-Propanediamine or 1,4-Butanediamine Systems

The speciation diagrams for manganese(II) with en, pn and bn solution systems are shown in Figure 7a–c, respectively. A solution with an equimolar concentration of manganese(II) and ethylenediamine yields about 40% of [Mn(en)]$^{2+}$, 45% of ionic manganese(II) and 15% of the bis complex. Two molar equivalents of ethylenediamine and a molar equivalent of manganese yield about 35% of the bis-complex, 45% of the mono-complex and 20% of ionic manganese(II). A solution with an equimolar concentration of manganese(II) and 1,3-propanediamine yields about 70% of [Mn(pn)]$^{2+}$, 20% of ionic manganese(II) and 10% of the bis complex. Two molar equivalents of 1,3-propanediamine and a molar equivalent of manganese yield about 40% of the bis-complex and 60% of the mono-complex. Additionally, a solution with an equimolar concentration of manganese(II) and 1,4-butanediamine yields about 70% of [Mn(bn)]$^{2+}$, 20% of ionic manganese(II) and 10% of the bis complex. Two molar equivalents of 1,4-butanediamine and a molar equivalent of manganese yield about 40% of the bis-complex, 60% of the mono-complex and 20% of ionic manganese(II). There is an increase in the abundance of [Mn(en)]$^{2+}$ to [Mn(pn)]$^{2+}$, possibly due to the
chelate effect. Nevertheless, there is a decrease in the abundance of \([\text{Mn(bn)}]^2+\), possibly due to chain length in which the chelate effect might decrease. An analogous behavior was reported before in the 1,4-butanediamine complexes with Ca\(^{2+}\) [20]. This effect can be comparable considering that Ca\(^{2+}\) and Mn\(^{2+}\) are very similar, since both are hard acids [44].

Figure 7. (a) Formation curves of the manganese(II)-ethylenediamine system in methanol. \([\text{Mn}]^{2+} = 0.3 \text{ mM}\) and ethylenediamine range from 0.03 to 0.6 mM. (b) Formation curves of the manganese(II)-1,3-propanediamine system in methanol. \([\text{Mn}]^{2+} = 0.288 \text{ mM}\) and 1,3-propanediamine range from 0.0288 to 0.576 mM. (c) Formation curves of the manganese(II)-1,4-butanediamine system in methanol. \([\text{Mn}]^{2+} = 0.16 \text{ mM}\) y 1,4-butanediamine range from 0.032 to 0.64 mM.

3. Experimental Section
3.1. Materials, Physical Measurements and Methods

For determination of the formation constants, Methanol HPLC grade (Fermont, Mexico) was used as a solvent; manganese(II) nitrate tetrahydrate Mn(NO\(_3\))\(_2\)-4H\(_2\)O (Sigma-Aldrich, St. Louis, MO, USA), ethylenediamine (Sigma-Aldrich, St. Louis, MO, USA), 1,3-propanediamine (Sigma-Aldrich, St. Louis, MO, USA) and 1,4-butanediamine (Sigma-Aldrich, St. Louis, MO, USA) were analytical grade and used without further purification. All spectral measurements were recorded using a quartz cell with 1 cm path length and 3 mL volume in a Shimadzu UV-vis-1800 spectroscopy system equipped with a Thermo Scientific thermostat system TPS-1500W, at 293 K. For the determination of formation constants, the analyzed spectral region was from 220 to 320 nm for all the experiments. The spectrophotometric data obtained were fitted with the software HypSpec [45]. To calculate the distribution diagrams of species, the software Hyperquad Simulation and Speciation (HySS2009) [46] was used, using the same methodology reported before [21]. In a typical spectral measurement of the manganese(II)-ligand complexes, stock solutions of manganese(II) and ligand (either ethylenediamine, 1,3-propanediamine or 1,4-butanediamine) were prepared and diluted to obtain a solution behaving according the Lambert–Beer law.
The final concentration of the Mn(II) ion was kept as constant; the concentration of the ligand was varied within a range. This process was repeated twice, each experiment being carried out at a different concentration of Mn(II) ion and at two different ranges of ligand concentration.

3.2. Equilibrium Studies of the Manganese(II) with Ethylenediamine, 1,3-Propanediamine and 1,4-Butanediocamine

For the manganese(II)–ethylenediamine system, two different stock solutions of ethylenediamine (1.80 or 3.00 mM) and Mn(NO$_3$)$_2$·4H$_2$O (1.60 and 3.00 mM) were prepared. In each experiment, the final concentration of manganese(II) remained constant at 0.160 and 0.300 mM, where the ethylenediamine concentrations were varied from 0.054 to 0.344 mM and 0.120 to 0.570 mM, respectively. A total of 33 spectra were used for the refinement. For the manganese–1,3-propanediamine system, stock solutions of 1,3-propanediamine (1.44 and 2.88 mM) and Mn(NO$_3$)$_2$·4H$_2$O (1.44 and 2.88 mM) were prepared. In each experiment, the final manganese(II) concentration remained constant at 0.144 and 0.288 mM; the 1,3-propanediamine concentrations were varied from 0.014 to 0.273 mM and from 0.028 to 0.547 mM, respectively. A total of 37 spectra were used for the refinement. For the manganese–1,4-butanediocamine system, stock solutions of 1,4-butanediocamine (1.60 and 3.20 mM) and Mn(NO$_3$)$_2$·4H$_2$O (1.60 and 3.20 mM) were prepared. In each experiment, the final manganese(II) concentration was set constant at 0.16 and 0.32 mM; the 1,4-butanediocamine concentrations were varied from 0.016 to 0.272 mM and from 0.032 to 0.512 mM, respectively. A total of 33 spectra were used for refinement.

4. Conclusions

The manganese complexes reported in this study show a spectral pattern that could be related to the chelate effect in which the molar absorbance is not directly related to the increase in the carbon chain of the ligand. The chelate effect may possibly decrease if the 1,4-butanediocamine is used as ligand in the manganese complex. The mono- and bis-complexes with manganese(II) and ethylenediamine and 1,3-propanediamine might have a similar geometry. In order to understand this behavior and determine the true geometry of the complexes, a crystallographic study should be conducted. Testing several ligands will allow us to understand some spectral properties of the manganese complexes and possibly propose a ligand to promote an accurate model complex and mimic the electronic spectra of the oxygen-evolving complex at photosynthesis II.

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