Ligation of water to magnesium chelates of biological importance

Dorota Rutkowska-Zbik · Małgorzata Witko · Leszek Fiedor

Received: 15 December 2011 / Accepted: 3 May 2012 / Published online: 29 May 2012 © The Author(s) 2012. This article is published with open access at Springerlink.com

Abstract Water binding to several Mg²⁺ chelates, ethylenediamine, ethylenediamine-N,N'-diacetate, porphyrin, chlorophyll a and bacteriochlorophyll a, to form five- and six-coordinate complexes is studied by means of density functional theory. The results obtained for magnesium chelates are compared with the properties of the respective aqua complexes and the influence of the permittivity of environment on the ligand binding energies is discussed. Although the most common coordination number of Mg²⁺ is six, in the tetrapyrrolic chelates it is reduced to five because the accommodation of the sixth water ligand results in no gain in energy. This is in line with the experimental observations made for coordination of chlorophylls in vivo. The binding between Mg²⁺ and water is mostly of electrostatic nature, which is supported by the finding that its energy is correlated both with the electron density of the chelator and with electrostatic potential determined at the ligand binding site.

Keywords Chlorophylls · DFT · Magnesium chelates · Porphyrins · Water

Introduction

Magnesium is one of the most ubiquitous metal ions in biological systems, whose role is to stabilize structures of proteins, lipid membranes, nucleotides and the nucleic acids. The stabilization is achieved by coordination of various ligands to the Mg²⁺ ion and the energy of the ligand-Mg²⁺ interactions provides the stability of the complexes. Also, Mg²⁺ is bound as the central metal ion in chlorophylls (Chls), the major photosynthetic pigments, in which it is chelated equatorially by the tetrapyrrolic macrocycle. This type of chelation does not satisfy the coordination sphere of the central Mg²⁺ ion and creates a coordination center, which can host up to two axial ligands. Thus, a coordinate bond, mainly to histidine residue, is the strongest interaction that stabilizes the structures of most photosynthetic pigment-protein complexes [1].

The coordination properties of the Mg²⁺ ion have been extensively studied both by experiment [1–5] and theory [6–13]. The most recent reviews of the theoretical investigation of the subject may be found in [14–17]. The ionic radius of the Mg²⁺ ion is relatively small (0.86 Å) and according to Pearson’s classification [18], it belongs to hard ions. As such, it forms stable complexes with O-donors, while the complexes with N-donors are somewhat less stable. In biological systems there are many types of potential ligands of Mg²⁺, such as carboxylic groups (aminoacid residues in polypeptides), carbonyl groups (from polypeptide backbone, aspartagine and glutamine), amine groups (from protein backbone and lysine), imidazole moiety (from histidine), phosphate groups (in nucleotides, nucleic acids and lipids), and water molecules.

The crystallographic data base survey reveals that the preferred coordination number of Mg²⁺ is six, however the structures in which Mg²⁺ accommodates higher coordination...
The influence of the nature of the environment on the structural properties of the central Mg$^{2+}$ in tetrapyrroles is more expanded, electron-rich and polarizable than tetrapyrroles. This discrepancy might be attributed to the fact that tetrapyrroles are more expanded, electron-rich and polarizable molecules than tetrapyrroles. Furthermore, it is known that the structure of the magnesium complexes in proteins (with acidic and neutral ligands) depends on the permittivity of the environment, what has been reviewed in details in Ref. [14]. The influence of the nature of the environment on the structural properties of the central Mg$^{2+}$ ion in tetrapyrroles has not been addressed straightforward so far. While Ryde et al. [9] report their structures as calculated in solvent through COSMO model, Ruiz-Lopez and co-workers take no environment into consideration [11] but include one explicit water molecule interacting with H$_2$O coordinated to the central magnesium ion [12].

The reasons for the observed mismatch in Mg$^{2+}$ behavior numbers are also known [19]. The coordination number of the central Mg$^{2+}$ ion in magnesium porphyrins and chlorophylls in free state (solution) can be either 5 or 6, depending on the ligand strength [3]. However, for Chls in vivo (bound to proteins) it rarely exceeds five [20, 21] but a six-coordinated species was also found, e.g., in the photosynthetic antenna LH1 [2]. Interestingly, to the best of our knowledge, the species with no axial ligand or with two axially ligated water molecules were never reported [1].

The reasons for the observed mismatch in Mg$^{2+}$ behavior have already been addressed, but as yet no consistent explanation of the experimental observations was proposed. Based on the experimental results, Kania and Fiedor attribute the lack of six-coordination in Chls to a drastic change of the hardness of the central Mg$^{2+}$ in the chelate [22]. Ryde et al. suggest that the binding of the sixth bio-ligand would not provide any gain in energy and therefore it is thermodynamically unprivileged [9]. In a recent theoretical study, Ruiz-Lopez et al. argue that the dispersion interactions play the major role in the interactions between magnesium and axial ligands in tetrapyrrolic systems and hence are the key factors controlling the axial ligation [11].

The influence of the nature of the environment on the structural properties of the central Mg$^{2+}$ ion in tetrapyrroles has not been addressed straightforward so far. While Ryde et al. [9] report their structures as calculated in solvent through COSMO model, Ruiz-Lopez and co-workers take no environment into consideration [11] but include one explicit water molecule interacting with H$_2$O coordinated to the central magnesium ion [12].

In view of the above, it becomes very relevant to find out how chelation of Mg$^{2+}$ ion by various chelating agents, not only of tetrapyrrolic type, affects its ligand binding properties. The aim of the present study is to examine in depth the electronic interactions of the studied structures and was further confirmed with vibrational analysis. The reported electronic energies were corrected for zero-point vibrational energy. The resolution-of-identity (RI) algorithm was applied in order to accelerate computation [30, 31]. All-electron Gaussian type orbitals of def-TZVP quality were used to define atomic orbitals [32]. The solvation was accounted for by COSMO model [33] with default radii for the elements (H=1.30, C=2.00, N=1.83, O=1.72) and 2.00 Å for magnesium. Three $\varepsilon$ values ($\varepsilon=4$, 20, 80) are used in order to take into account the nature of the possible environment in which magnesium ion is located. The low permittivity ($\varepsilon=4$) represents a non-polar environment, such as the buried cavity in protein interior, higher $\varepsilon$ value (20) relates to the cavity, which is more exposed to water, whereas the largest value represents the aqueous environment. The electronic structures of the investigated species are additionally elucidated by means of Mulliken population analysis [34]. The present results were obtained with Turbomole v. 6.3 [35].
Results and discussion

Reference systems: [Mg(H$_2$O)$_5$]$^{2+}$ and [Mg(H$_2$O)$_6$]$^{2+}$

In order to check the appropriateness of the theoretical methodology used in the present study, first the geometry and electronic structure of the five- and six-coordinate magnesium aqua complexes have been calculated – see Table 1. [Mg(H$_2$O)$_5$]$^{2+}$ exhibits slightly distorted square-based pyramid geometry with all magnesium–water distances falling in the range of 2.06-2.08 Å. All Mg-water distances in octahedral [Mg(H$_2$O)$_6$]$^{2+}$ are equal to 2.13 Å, c.a. 0.05 Å more than the Mg-H$_2$O distances found in the crystal structures of hexaaqua magnesium species [36]. The reported binding energies (see Table 1) are calculated according to the formulae:

$$\Delta E = E_{\text{tot}}\left([\text{Mg(H}_2\text{O)}_5]^{2+}\right) - E_{\text{tot}}\left([\text{Mg(H}_2\text{O)}_4]^{2+}\right) - E_{\text{tot}}(\text{H}_2\text{O})$$

and the sixth ligand:

$$\Delta E = E_{\text{tot}}\left([\text{Mg(H}_2\text{O)}_6]^{2+}\right) - E_{\text{tot}}\left([\text{Mg(H}_2\text{O)}_5]^{2+}\right) - E_{\text{tot}}(\text{H}_2\text{O})$$

The binding energy of the fifth and sixth water in the gas phase amounts to -29.4 and -26.7 kcal mol$^{-1}$, respectively. These values are consistently higher by 3–4 kcal mol$^{-1}$ than the ones determined in an electrospray experiment [4].

The inclusion of the environment polarity through the COSMO model considerably lowers ligand binding energies. In water ($\varepsilon=80$) it is decreased by about 60 %.

Chelates of Mg$^{2+}$

The electronic and structural parameters of the studied chelates are listed in Table 2 (five-coordinate complexes) and Table 3 (six-coordinate complexes). Geometry structures of the obtained five-coordinate complexes are shown in Fig. 2. In six-coordinate systems magnesium ion exhibits octahedral coordination. A comparison of the calculated values of the Mg-H$_2$O bond lengths with the existing crystallographic

---

Table 1. Calculated properties of [Mg(H$_2$O)$_5$]$^{2+}$ and [Mg(H$_2$O)$_6$]$^{2+}$. Energies are in kcal mol$^{-1}$ and bond lengths in Å. Other published results are marked in italics:

| Complex       | $\Delta E$ (gas) | $\Delta E$ ($\varepsilon=4$) | $\Delta E$ ($\varepsilon=20$) | $\Delta E$ ($\varepsilon=80$) | r(Mg - H$_2$O) |
|---------------|------------------|------------------------------|------------------------------|------------------------------|----------------|
| [Mg(H$_2$O)$_5$]$^{2+}$ | -29.4; -28.2B3LYP, -29.4MP2; a exp 25.5±1.3 b | -18.4 | -10.9 | -9.7 | 2.06 - 2.08 |
| [Mg(H$_2$O)$_6$]$^{2+}$ | -26.7; -25.4B3LYP, -29.1MP2; a exp 23.5±1.6 b | -15.6 | -12.8 | -11.8 | 2.13 |

a: Other published results; b: Experimental bond lengths.
and/or already published theoretical parameters is not possible for all of the investigated structures due to the lack of the appropriate data. The length of the Mg-H2O bond in [Mg(EDTA)(H2O)] is equal to 2.06 Å [19], which is shorter than the values reported in the present survey for the EDDA complexes (2.14 and 2.21 Å for the five- and six-coordinate, respectively). The computed here magnesium–water distances in all tetrapyrrolic systems are in good agreement with existing experimental and theoretical values (Tables 2 and 3). In the crystal structure of the five-coordinate [Mg(Por)(H2O)] complex it amounts to 2.10 Å [37]. In five-coordinate water adducts to Chla, the Mg-H2O bond length spans from 1.87 to 2.50 Å [38, 39], owing to the low resolution. Theoretical calculations at the DFT-BP/Ri level by Heimdal et al. [9] give 2.18 and 2.16 Å for Chla and BChla, respectively, as compared with 2.19 and 2.17 Å obtained in the present study. Ben Fredj and co-authors [11] report 2.16 and 2.24 Å for five- and six-coordinate porphyrin complexes calculated at the DFT-B3LYP level, respectively, which is slightly shorter than 2.20 and 2.26 Å reported here. As already mentioned, no crystal structures of six-coordinate water complexes of Por, Chla and BChla are known as probably no such forms exist in nature [2].

When water molecule is coordinated by magnesium chelate to form both five- and six-coordinate adducts, the Mg-H2O bond is longer than the one in the reference aqua complexes. The elongation is proportional to the electron density of the ligand chelating the central ion and changes in the row: EN<EDDA<BChla<Chla<Por. Not surprisingly, the decrease of the Mg-H2O bond energy follows the same trend. The strongest Mg-H2O bond is found in the EDDA chelates, while the weakest is in Por complex. Thus, the bond strength of Mg-H2O in the five- and six-coordinate systems is diminished as compared to the respective aqua complexes.

Irrespective of the polarity of the environment, water binding is always thermodynamically privileged in five-coordinate complexes. In all studied chelates H2O binding energies are negative and in the range of typical dative water–metal bonds. As in the case of the aqua structure, Mg-H2O bond is weakened by 56 – 36 % (for EN and BChla, respectively) when changing from the gas phase to the aqueous solution.

| L      | n | q | ΔE (gas) | ΔE (ε=4) | ΔE (ε=20) | ΔE (ε=80) | Mg-H2O |
|--------|---|---|----------|----------|-----------|-----------|--------|
| EN     | 2 | +2| −21.7    | −13.7    | −10.3     | −9.6      | 2.13   |
| EDDA   | 1 | 0 | −17.3    | −11.6    | −8.8      | −8.2      | 2.14   |
| BChla  | 1 | 0 | −11.7    | −9.0     | −7.8      | −7.5      | 2.17   |
| Chla   | 1 | 0 | −11.0    | −8.3     | −7.1      | −6.9      | 2.19   |
| Por    | 1 | 0 | −10.2    | −7.4     | −6.3      | −6.0      | 2.20   |

Table 3 Water binding energies (in kcal mol⁻¹) to five-coordinate complexes of [Mg(L)n(H2O)]⁴⁺ type determined at BP/def-TZVP level and Mg-H2O bond lengths (in Å). Other published results are marked in italics:

| L      | n | q | ΔE (gas) | ΔE (ε=4) | ΔE (ε=20) | ΔE (ε=80) | Mg-H2O |
|--------|---|---|----------|----------|-----------|-----------|--------|
| EN     | 2 | +2| −17.6    | −9.1     | −5.4      | −4.6      | 2.24   |
| EDDA   | 1 | 0 | −8.8     | −3.9     | −1.6      | −1.0      | 2.21 exp. 2.21⁶|
| BChla  | 1 | 0 | −6.4     | −2.3     | −0.4      | 0.0       | 2.26   |
| Chla   | 1 | 0 | −6.0     | −1.5     | 0.6       | 1.0       | 2.28; 2.29 |
| Por    | 1 | 0 | −2.7     | −1.1     | 0.6       | 1.0       | 2.30   |

---

* Springer
but still remains in the region of thermodynamically stable bonds.

The situation is somewhat different when considering six-coordinate structures. In gas phase, the electronic energy of water binding as the sixth ligand is always negative, indicating the ability to form the six-coordinate structures. The picture is changed when the environment is included in the theoretical model. The sixth ligand binding energy becomes either small, for EN and EDDA, or positive, in the case of tetrapyrrole chelators. Interestingly, six-coordinate tetrapyrrolic adducts do not tend to be formed even in environments of very low polarity ($\varepsilon = 4$). This may provide an explanation for the notion that these structures are rarely found in reality - there is no net gain in energy of the whole system upon formation of six-coordinate adducts of these types.

Additionally, one should bear in mind that in aqueous media water molecules are connected by a net of hydrogen bonds. Theoretical calculations on the structure of water indicate that each H$_2$O molecule forms 3.6 H-bonds on average [40–42]. The formation of another bond, such as with magnesium ion, would require breaking of at least one of these, with energetic penalty as high as 3–5 kcal mol$^{-1}$. Also, in some cases, the bond formation might not be favored from the thermodynamic point of view, which was already discussed for magnesium [8]. As seen from experiment, an easy interchange of water molecules within its first and second coordination sphere is also observed for the simple hexaaqua magnesium complex [4]. At higher temperatures, the six-coordinate aqua complex undergoes relatively easy transformation to the four-coordinate species with two water molecules in the second coordination shell.

In view of the determined order of the decreasing binding ability of H$_2$O ligand, i.e., EN < EDDA < BChla < Chla < Por, which correlates with the increasing electron density of the chelating ligand, it appears that electrostatic field of Mg chelates plays an important role in the binding of H$_2$O. To assess this possibility, Mulliken and Merz-Kollman population analyses have been performed and an electrostatic potential in the same position as O atom from water ligand has been computed (water ligand was removed whereas the geometry of the rest of the system was frozen). The analysis reveals that the charge on magnesium ion and water ligands does not vary in the series of the studied complexes. The Mg charge falls in the range 1.32 - 1.36 (Mulliken) or 0.77 – 0.89 (MK), while water molecules bear net positive charge (0.06 – 0.09 according to Mulliken, and 0.02 – 0.06 according to MK). The Mg ion interacts directly with negatively charged O atoms ($\approx -0.60 - -0.51$ – Mulliken, -0.86 - -0.91 - MK). The Mg-H$_2$O binding energies correlate with the size of negative charge accumulated on O. The electrostatic potential at the site occupied by water molecule in the six-coordinate complex is highly positive in the EN and EDDA adducts (0.39 and 0.48 a.u., respectively). In Chla and BChla, the electrostatic potential is lower (0.24 a.u. in each) and so are the Mg-H$_2$O binding energies. For the Por complex, however, the calculated electronic potential is neutral (0.00 a.u.), not fostering the effective interaction between Mg and water. This observation is further reflected by the lowest binding energy.

All in all, it is found that for all neutral complexes water binding energies correlate with the electrostatic potentials – the correlation coefficient for the relationship is 0.99. This indicates that in this type of compounds electrostatics would prevail in Mg-H$_2$O bonding, implying strong ionic character of the bonding. Moreover, the strength of the Mg-H$_2$O bond is largely influenced by the interaction between H$_2$O and chelator, in particular by its electronic structure. It might arise from two factors. One may be the overall electron density of the atoms forming the immediate surrounding of Mg$^{2+}$, here, e.g., the type of the basic tetrapyrrole ring: porphyrin, chlorin (Chla), bacteriochlorin (BChla). The second is due to the presence of the substituting groups, which are further apart, but due to their polarity, may largely influence the electrostatic potential at the ligand binding site.

Conclusions

1. Mg-H$_2$O bond is longer and weaker in chelates than in the respective aqua complexes. The bond elongation and the decrease of binding energy is proportional to the electron density of the chelating ligand around the central ion and change in the following order: EN < EDDA < BChla < Chla < Por, which correlates with the increasing electron density of the chelating ligand, it appears that electrostatic field of Mg chelates plays an important role in the binding of H$_2$O. To assess this possibility, Mulliken and Merz-Kollman population analyses have been performed and an electrostatic potential in the same position as O atom from water ligand has been computed (water ligand was removed whereas the geometry of the rest of the system was frozen). The analysis reveals that the charge on magnesium ion and water ligands does not vary in the series of the studied complexes. The Mg charge falls in the range 1.32 - 1.36 (Mulliken) or 0.77 – 0.89 (MK), while water molecules bear net positive charge (0.06 – 0.09 according to Mulliken, and 0.02 – 0.06 according to MK). The Mg ion interacts directly with negatively charged O atoms ($\approx -0.60 - -0.51$ – Mulliken, -0.86 - -0.91 - MK). The Mg-H$_2$O binding energies correlate with the size of negative charge accumulated on O. The electrostatic potential at the site occupied by water molecule in the six-coordinate complex is highly positive in the EN and EDDA adducts (0.39 and 0.48 a.u., respectively). In Chla and BChla, the electrostatic potential is lower (0.24 a.u. in each) and so are the Mg-H$_2$O binding energies. For the Por complex, however, the calculated electronic potential is neutral (0.00 a.u.), not fostering the effective interaction between Mg and water. This observation is further reflected by the lowest binding energy.

2. The formation of five-coordinate Mg-H$_2$O complexes is thermodynamically favorable, in contrast to the formation of six-coordinate complexes, in agreement with the fact that the six-coordinate complexes of Por, Chla and BChla with water are uncommon.

3. The analysis of the factors influencing Mg-H$_2$O bonding shows that the strength of Mg-H$_2$O bond correlates with
the negative charge of oxygen atom and the electrostatic potential at the ligand binding site. These observations lead to the conclusion that the bond between magnesium and water is mostly of electrostatic nature.

4. Water binding energies are lowered (with respect to their values in the gas phase) in all the systems when the polarity of environment is taken into account in the calculations through its dielectric constant. The higher the dielectric constant the weaker the magnesium - water bond.

Acknowledgments The work was in part supported by the Ministry of Science and Higher Education within the project No: N N204 439640 in years 2011–2014 (D.R.-Z. and M.W.) and in part by a research grant from the Foundation for Polish Science (TEAM/2010-5/3 to L.F.). The Faculty of Biochemistry, Biophysics and Biotechnology of the Jagiellonian University is a beneficiary of the structural funds from the European Union (grant No: POIG.02.01.00-12-064/08 – “Molecular biotechnology for health”).

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

1. Brindell M, Stawoska I, Orzel L, Labuz P, Stochel G, van Eldik R (2008) Application of high pressure laser flash photolysis in studies on selected hemoprotein reactions. Biochim Biophys Acta 1784 (11):1481–1492. doi:10.1016/j.bbabio.2008.08.006
2. Fiedor L, Kania A, Mysiwa-Kurdziel B, Orzel L, Stochel G (2008) Understanding chlorophylls: central magnesium ion and phytyl as structural determinants. Biochim Biophys Acta 1777 (12):1491–1500. doi:10.1016/j.bbabio.2008.09.005
3. El Alaoui El Abdallaoui H, Champmartin D, Rubini P (2001) Complexes of EDTA in aqueous solutions. Structural aspects from a 13 C NMR relaxation study. J Chem Soc, Dalton Trans (14):2153–2156. doi:10.1039/b101289o
4. Rodriguez-Cruz SE, Jockusch RA, Williams ER (1999) Hydration energies and structures of alkaline earth metal ions, M2+(H2O)n, n = 5–7, M Mg, Ca, Sr, and Ba. J Am Chem Soc 121(38):8898–8906. doi:10.1021/ja9911871
5. Drzewiecka-Matuszek A, Skalna A, Karocki A, Stochel G, Fiedor L (2005) J Biol Inorg Chem 10:453–462
6. Dudev T, Lim C (1999) Incremental binding free energies in Mg2+ complexes: a DFT study. J Phys Chem A 103(40):8093–8100. doi:10.1021/jp991575p
7. Dudev T, Lim C (2000) Metal binding in proteins: the effect of the dielectric medium. J Phys Chem B 104(15):3692–3694. doi:10.1021/jp9914559
8. Dudev T, Lin YL, Dudev M, Lim C (2003) First-second shell interactions in metal binding sites in proteins: a PDB survey and DFT/CDM calculations. J Am Chem Soc 125(10):3168–3180. doi:10.1021/ja029722z
9. Heimdal J, Jensen K, Devarajan A, Ryde U (2007) The role of axial ligands for the structure and function of chlorophylls. J Biol Inorg Chem 12(1):49–61. doi:10.1007/s00775-006-0164-z
10. Bock CW, Kaufman Katz A, Glusker JP (1995) Hydration of zinc ions: a comparison with magnesium and beryllium ions. J Am Chem Soc 117(13):3754–3765
11. Ben Fredj A, Ben Lakhdar Z, Ruiz-López MF (2009) Six-coordination in chlorophylls: the fundamental role of dispersion energy. Chem Phys Lett 472(4–6):243–247. doi:10.1016/j.cplett.2009.03.025
12. Fredj AB, Ruiz-Lopez MF (2009) Theoretical study of chlorophyll a hydrates formation in aqueous organic solvents. J Phys Chem B 114(1):681–687. doi:10.1021/jp909380t
13. Dudev T, Cowan JA, Lim C (1999) Competitive binding in magnesium coordination chemistry: water versus ligands of biological interest. J Am Chem Soc 121(33):7665–7673. doi:10.1021/ja984470t
14. Dudev T, Lim C (2003) Principles governing Mg, Ca, and Zn binding and selectivity in proteins. Chem Rev 103(3):773–787. doi:10.1021/cr020467n
15. Dudev M, Lim C (2007) Effect of carboxylate-binding mode on metal binding/selectivity and function in proteins. Acc Chem Res 40:85–93
16. Linnanto J, Korppi-Tommola J (2006) Quantum chemical simulation of excited states of chlorophylls, bacteriochlorophylls and their complexes. Phys Chem Chem Phys 8(6):663–687
17. SantaLucia J, Hicks D (2004) The thermodynamics of DNA structural motifs. Annu Rev Biophys Biomol Struct 33(1):415–440. doi:10.1146/annurev.biophys.32.110601.141800
18. Pearson RG (1963) Hard and soft acids and bases. J Am Chem Soc 85(22):3533–3539. doi:10.1021/ja00905a001
19. Stezowski JJ, Countryman R, Hoard JL (1973) Structure of the ethylenediaminetetracetatoaquomagnesate(II) ion in a crystalline sodium salt. Comparative stereochemistry of the seven-coordinate chelates of magnesium(II), manganese(II), and iron (III). Inorg Chem 12(8):1749–1754. doi:10.1021/ic50126a009
20. Oba T, Tamaki H (2002) Which side of the π-macrocycle plane of (bacterio)chlorophylls is favored for binding of the fifth ligand? Photosynth Res 74(1):1–10. doi:10.1021/jp909380t
21. Balaban TS, Fromme P, Holzwarth AR, Kraushaer K, Fazakerley DJ (2002) Relevance of the diastereotopic ligation of magnesium atoms of chlorophylls in Photosystem I. Biochim Biophys Acta 1556(2–3):197–207. doi:10.1016/s0005-2728(02)00363-8
22. Kania A, Fiedor L (2005) Steric control of bacteriochlorophyll ligation. J Am Chem Soc 128(2):454–458. doi:10.1021/ja045537x
23. Garmer DR, Gresh N (1994) A comprehensive energy component analysis of the interaction of hard and soft dicationics with biological ligands. J Am Chem Soc 116(8):3556–3567. doi:10.1021/ja00087a049
24. Gresh N, Garmer DR (1996) Comparative binding energetics of Mg2+, Ca2+, Zn2+, and Cd2+ to biologically relevant ligands: combined ab initio SCF supermolecule and molecular mechanics investigation. J Comput Chem 17(12):1481–1495. doi:10.1002/(sici)1096-987x(19960917)12:1481:aidd-7c>3.0.co;2-g
25. Dirac PAM (1929) Quantum mechanics of many-electron systems. Proc R Soc Lond Ser A 123(792):714–733. doi:10.1098/ rspa.1929.0094
26. Slater JC (1951) A simplification of the hartree-fock method. Phys Rev 81(3):385–390
27. Vosko SH, Wilk L, Nusair M (1980) Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Can J Phys 58(8):1200–1211. doi:10.1139/p80-159
28. Becke AD (1988) Density-functional exchange-energy approximation with correct asymptotic behavior. Phys Rev A 36(6):3098–3100
29. Perdew JP (1986) Density-functional approximation for the correlation energy of the inhomogeneous electron gas. Phys Rev B 33(12):8822–8824
30. Eichkorn K, Teutleri O, Ohm H, Häser M, Ahlrichs R (1995) Auxiliary basis sets to approximate coulomb potentials. Chem Phys Lett 240:283–289
31. Eichkorn K, Weigend F, Treutler O, Ahlrichs R (1997) Theor Chem Acc 97:119–124
32. Schäfer A, Huber C, Ahlrichs R (1994) Fully optimized contracted gaussian basis sets of triple zeta valence quality for atoms Li to Kr. J Chem Phys 100(8):5829–5835
33. Klamt A, Schuurmann G (1993) COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. J Chem Soc Perkin Trans 2 (5):799–805
34. Mulliken RS (1955) Electronic population analysis on LCAO[Single Bond]MO molecular wave functions. I. J Chem Phys 23(10):1833–1840. doi:10.1063/1.1740588
35. TURBOMOLE V6.3 (2011) adoUoKa, Forschungszentrum Karlsruhe GmbH, TURBOMOLE GmbH saf, http://www.turbomole.com
36. Julian MOD, Day VW, Hoard JL (1973) Structure of hexaquomagnesium dihydrogenethylenediaminetetraacetate, Mg(OH2)6H2EDTA. Stereochemistry of the uncomplexed H2EDTA2- ion. Inorg Chem 12(8):1754–1757. doi:10.1021/ic50126a010
37. Timkovich R, Tulinsky A (1969) Structure of aqumagnesium tetraphenylporphyrin. J Am Chem Soc 91(16):4430–4432. doi:10.1021/ja01044a018
38. Liu Z, Yan H, Wang K, Kuang T, Zhang J, Gui L, An X, Chang W (2004) Crystal structure of spinach major light-harvesting complex at 2.72[Å] resolution. Nature 428 (6980):287–292. http://www.nature.com/nature/journal/v428/n6980/supinfo/nature02373_S1.html
39. Jordan P, Fromme P, Witt HT, Klukas O, Saenger W, Krausz N (2001) Three-dimensional structure of cyanobacterial photosystem I at 2.5[Å][angstrom] resolution. Nature 411(6840):909–917. http://www.nature.com/nature/journal/v411/n6840/supinfo/411909a0_S1.html
40. Buch V, Sandler P, Sadlej J (1998) Simulations of H2O solid, liquid, and clusters, with an emphasis on ferroelectric ordering transition in hexagonal ice. J Phys Chem B 102(44):8641–8653. doi:10.1021/jp980866f
41. Buck U, Ettischer I, Melzer M, Buch V, Sadlej J (1998) Structure and spectra of three-dimensional (H_{2}O)_{n} Clusters, n=8,9,10. Phys Rev Lett 80(12):2578–2581
42. Smith JD, Cappa CD, Wilson KR, Cohen RC, Geissler PL, Saykally RJ (2005) Unified description of temperature-dependent hydrogen-bond rearrangements in liquid water. Proc Natl Acad Sci USA 102(40):14171–14174