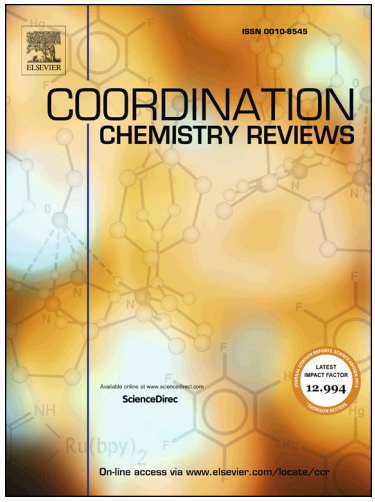

Review

Protonation equilibria of transition metal complexes: from model systems toward the Mn-complex in photosystem II

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PII: S0010-8545(17)30038-3
DOI: http://dx.doi.org/10.1016/j.ccr.2017.02.017
Reference: CCR 112405

To appear in: *Coordination Chemistry Reviews*

Received Date: 30 January 2017
Revised Date: 17 February 2017
Accepted Date: 21 February 2017

Please cite this article as: E. Rossini, E-W. Knapp, Protonation equilibria of transition metal complexes: from model systems toward the Mn-complex in photosystem II, *Coordination Chemistry Reviews* (2017), doi: http://dx.doi.org/10.1016/j.ccr.2017.02.017

Protonation equilibria of transition metal complexes: from model systems toward the Mn-complex in photosystem II

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Abstract

We report state-of-the-art pK_A computations of manganese model systems. The employed methods can be used to perform pK_A computations on the oxygen evolving Mn_4CaO_5 cluster (OEC) in photosystem II (PSII). These computations are very useful for understanding the function of molecular machines and nano-structures considered for artificial photosynthesis. We first summarize the activities going on in natural and artificial photosynthesis. Next, it is outlined how OEC and manganese model structures can vary with different protonation and oxidation states. We also discuss the role of the dielectric constant of proteins in electrostatic energy computations. Then the results obtained so far on pK_A computations of the OEC are summarized. Subsequently, we outline the theoretical background behind performing *ab initio* pK_A value computations. In the application part, we first consider pK_A computations for the simple hexa-aqua manganese complex. There it is discussed in detail how computed pK_A values depend on atomic radii, charges and the electron leakage effect. A presentation of results follows including a critical discussion of the computed pK_A values of di-manganese model complexes. Possible reasons for deviations from measured pK_A values and techniques for improvement are discussed and summarized in a final section.

Keywords: natural photosynthesis; artificial photosynthesis; pK_A computations; solvation energy; electron leakage; hexa-aqua manganese; di-manganese complexes; electrostatic constant; electrostatic energy computations; atomic partial charges; Poisson equation; DFT with B3LYP;

Abbreviations:
COSMO, conductor-like screening model; COSMO-RS, conductor-like screening model for real solvents; CPCM, conductor-like polarizable continuum model; DBLOC, d-block localized orbital correction; DFT, density functional theory; EXAFS, extended X-ray absorption fine structure; MEAD, macroscopic electrostatics with atomic detail; OEC, oxygen evolving complex; PBF, Poisson-Boltzmann finite element solver; PCET, proton coupled electron transfer; RPC, redox-proton coupling, PSII, photosystem II; RESP, restrained electrostatic potential; SAWYEU, di-manganese complex $[Mn(\mu\text{–}O)(2,2'\text{-bipyridyl})_2]_2$; SOZMUP, di-manganese complex $[Mn(\mu\text{–}O)(N,N'\text{-bis(salicylidene)-1,3-propanediamine})]_2$; SCF, self-consistent field; SES, solvent excluded surface;