Chapter 10

The Catalytic Manganese Cluster: Organization of the Metal Ions

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Summary

The light-induced oxidation of water to O\textsubscript{2} is catalyzed by a four-manganese atom cluster associated with Photosystem II (PS II). This chapter summarizes ongoing investigations of the oxidation state, the structure and the associated cofactors calcium and chloride of the catalytic Mn cluster using X-ray and electron paramagnetic resonance (EPR) spectroscopy. Manganese K-edge X-ray spectroscopy, K\textsubscript{3} X-ray emission spectroscopy (XES), and extended X-ray absorption fine structure (EXAFS) studies have not only determined the oxida-

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tion states and structural features, but also changes that occur in oxidation state of the Mn cluster and in its structural organization during the accumulation of oxidizing equivalents leading to O$_2$ formation. Combining X-ray spectroscopy information with X-ray diffraction studies, and consistent with the available EPR data, we have succeeded in relating the range of likely structures of the Mn cluster. EXAFS studies at the strontium and calcium K-edges have provided evidence that the catalytic center is a Mn/Ca heteronuclear complex. Based on the X-ray spectroscopy data, models for the structure and a mechanism for O$_2$ evolution are presented.

I. Introduction

Most of the O$_2$ in the atmosphere that supports life on earth is generated by plants, algae, and cyanobacteria by the photo-induced oxidation of water to dioxygen:

$$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4e^- + 4\text{H}^+ \quad (1)$$

This reaction is catalyzed by a manganese/calcium complex (Mn$_n$Ca$_x$), which sequentially stores four oxidizing equivalents (i.e. the S$_n$ states, where n = 0 – 4) that are used to oxidize two molecules of water to molecular oxygen (Kok et al., 1970; for a review, see Joliot, 2003). The Mn complex is part of the multiprotein Photosystem II (PS II) assembly (Chapters 3–6), which contains the reaction center involved in photosynthetic charge separation (Chapter 7) and an antenna complex of chlorophyll molecules (Chapter 2). The assembly also contains cytochrome $b_{559}$ (Chapter 15) and a Fe-quinone electron acceptor complex (Chapter 8).

X-ray absorption spectroscopy (XAS) (Sauer et al., 1992; Robblee et al., 2001) and electron paramagnetic resonance (EPR) (Dismukes and Siderer, 1981; Messinger et al., 1997b; Britt et al., 2000) studies have emerged as the primary methods to provide structural and chemical information about the oxygen evolving complex (OEC) and devise a working model for its Mn cluster. XAS has been used to examine the structural environment of metal ions in many proteins (Cramer, 1988; Yachandra, 1995). The energy of the incoming X-ray photons and of the outgoing fluorescence is specific to the Mn atom; hence, other metals or the protein matrix normally co-purified with the OEC in a PS II preparation do not interfere. Element-specificity and applicability to non-crystalline samples have made X-ray spectroscopy a useful technique for probing the structure of the Mn complex in the complicated environment of PS II, which has many components such as non-heme iron, cytochrome, chlorophylls that interfere with other techniques. The structural studies can also be performed on crystals, or on frozen solutions and several of the S state intermediates mentioned above have been stabilized as frozen solutions and studied by X-ray spectroscopy. The different regions of the X-ray spectrum provide complementary information: X-ray absorption near edge spectroscopy (XANES) yield information about the oxidation states and site symmetry of the absorbing atom while extended X-ray absorption fine structure (EXAFS) is sensitive to distances, numbers, and atomic number of atoms around the absorbing atom. The more recently used technique of X-ray emission spectroscopy (XES) has also provided information regarding the identity of the oxidation states of Mn complex in the various S-states and the changes accompanying the S-state advance.

Critical questions related to the process of photosynthetic water oxidation are: (i) What are the oxidation state(s) and structural changes in the Mn complex as the OEC proceeds through the S-state cycle? and (ii) What is the mechanism by which four electrons are removed from two water molecules by the Mn complex to produce an O$_2$ molecule? Electron paramagnetic resonance (EPR) and X-ray spectroscopy studies and the interplay between these two methods have provided significant insights into the structure and the mechanism of the OEC. This chapter focuses on the application of X-ray spectroscopic techniques to resolve structural questions regarding the Mn cluster in the OEC, with emphasis on the results from our laboratory. Many excellent reviews are available for comprehensive surveys of the Mn complex and the OEC, EPR, and XAS literature (Debus, 1992; Rutherford et al., 1992; Britt, 1996;