Probing the S_0 State of Photsystem II with Isoelectrostatic Mixed-Valent Tetrameric Manganese Complexes

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Photosynthesis is essential to aerobic life on this planet. The photosynthetic system captures light energy which is then used to reduce carbon dioxide and water to form sugars in green plants and algae. In the process molecular oxygen is released into the environment. The enzyme which produces oxygen is known as photosystem II (PSII). At the heart of this enzyme is a tetrameric manganese cluster known as the oxygen evolving complex (OEC). The manganese cluster undergoes a series of oxidations in a reaction cycle with each different oxidation level known as an S state. The starting state, S_0, is the most reduced and the production of oxygen occurs upon the transition of the most oxidized states to S_0 ($S_3 \rightarrow S_4 \rightarrow S_0$). The exact oxidation states of each manganese ion in each S state is still highly debated. The oxidation states of the manganese ions for S_0 have been proposed as $Mn^{II}Mn^{III}Mn^{IV}_2$ or $Mn^{III}_3Mn^{IV}$. Both clusters have the same charge (13+) but have a different distribution of oxidation states. To probe the oxidation states of the manganese ions of S_0 and determine if different oxidation state distributions can be distinguished experimentally, we have synthesized four model complexes (two trimeric and two tetrameric) and have characterized them with X-ray absorption spectroscopy (XAS) and electron paramagnetic resonance (EPR). The two trimeric manganese clusters - $Mn^{II}Mn^{III}_2$ and $Mn^{II}_2Mn^{IV}$ (8+ charge) - can be clearly distinguished in XAS and EPR measurements. In addition, the two tetrameric manganese complexes - $Mn^{II}_2Mn^{III}_2$ and $Mn^{II}_3Mn^{IV}$ (10+ charge) – can be distinguished by XAS measurements. The use of these techniques may have consequences on the determination of the oxidation state distribution of S_0. We acknowledge the National Institute of Health (GM39406) for funding this research work.