

SYNTHESIS OF TETRANUCLEAR MANGANESE COMPLEXES AS
MODELS OF THE PHOTOSYNTHETIC WATER OXIDATION SITE

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We are engaged in a search for a tetranuclear manganese complex to function as a model of the photosynthetic water oxidation enzyme and to help elucidate various aspects of the oxygen evolution reaction. Synthetic procedures into the desired type of complex have been devised. Reaction in MeCN of the oxo-centered trinuclear species $[\text{Mn}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]^{0,+}$ (R = Me, Ph; L = a donor molecule) with 3 equiv of bipyridine (bipy) leads to high yield formation of $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CR})_x(\text{bipy})_2]^{y+}$ (1; R = Me, x = 6, y = 0; 2; R = Ph, x = 7, y = 0; 3; R = Me, x = 7, y = 1⁺). The three complexes contain average Mn oxidation states of +2.5, +2.75 and +3.0, respectively; the latter two correspond to the S_0 and S_1 enzyme oxidation states. The structure of 3 has been solved and shown to have a butterfly arrangement of the 4 Mn atoms with a $\mu_3\text{-O}^{2-}$ capping each wing and peripheral ligation from bridging OAc and terminal bipy groups.

Complex 1 has several features which correspond to those of the enzyme and which thus make it attractive as a potential model of S_1 : (i) a metal nuclearity of 4; (ii) oxide (O^{2-}) bridges between the Mn atoms; (iii) two types of inequivalent Mn atoms; (iv) structural parameters (Mn...Mn distances of 2.848 and 3.2-3.3Å and an EXAFS spectrum similar to that of the enzyme); and (v) peripheral ligation comprised of O- and N-based groups.

Reaction of $[\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_6](\text{O}_2\text{CMe})(\text{HO}_2\text{CMe})$ with Me_3SiCl in the presence of imidazole (HIm) leads to formation of $(\text{H}_2\text{Im})_2[\text{Mn}_4\text{O}_3(\text{O}_2\text{CMe})_3\text{Cl}_6(\text{HIm})]$ (4) (H_2Im = imidazolium cation), which has been structurally characterized. The structure consists of a Mn_4 pyramid with the basal plane capped by a $\mu_3\text{-Cl}^-$ and each vertical face capped by a $\mu_3\text{-O}^{2-}$. The three OAc⁻ groups each bridge a vertical edge, and the remaining five Cl⁻ and one HIm group function as terminal ligands to the basal Mn atoms. The central $\text{Mn}_4\text{O}_3\text{Cl}$ core could also be described as a severely distorted cube. The average metal oxidation state is +3.25 corresponding to the enzyme S_2 level. Like 3, this complex again has two types of Mn...Mn separations, ca. 2.81 and 3.2-3.3Å consistent with the EXAFS data on the enzyme. The complex is EPR active in DMF/toluene solution and shows extensive hyperfine detail; its overall appearance is reasonably similar to the S_2 EPR spectrum. Finally, the structures of complexes 1-4 have been incorporated into mechanistic proposals for how the water oxidation cycle is carried out, i.e., the structural identity of the various S_n states and mode of substrate transformation. This scheme employs the following oxidation state assignments: $S_0(\text{Mn}^{2+})$, $S_1(4 \times \text{Mn}^{3+})$, $S_2(3 \times \text{Mn}^{3+}, \text{Mn}^{4+})$, $S_3(2 \times \text{Mn}^{3+}, 2 \times \text{Mn}^{4+})$ and $S_4(\text{Mn}^{3+}, 3 \times \text{Mn}^{4+})$. The proposed mechanism is in accord with available data on the natural system, including pattern of H^+ loss and changes in cluster charge.