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A synthetic model for the oxygen-evolving complex in Sr$^{2+}$-containing photosystem II

Changhui Chen$^a$, Chunxi Zhang$^b$, Hongxing Dong$^a$, Jingquan Zhao$^b$

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A novel heterometallic MnSr complex containing Mn$_2$SrO$_4$ cuboidal moiety and all types of $\mu$-O$^2$ moieties observed in the oxygen-evolving complex (OEC) in Sr$^{2+}$-containing photosystem II (PSII) has been synthesized and characterized, which provides a new synthetic model for the OEC.

The oxygen-evolving complex (OEC) within photosystem II (PSII) of plants, algae and cyanobacteria serves as a nature’s blueprint for water splitting catalyst$^{1-5}$. The structure of OEC has been recently revealed by X-ray crystal structure of PSII (Fig. 1)$^{11-13}$. There are two unique characteristics in the structural motif of OEC. One is the incorporation of Ca$^{2+}$ within the Mn$_2$Ca$_4$ cubane through three $\mu$-oxido moieties. The other is the simultaneous presence of $\mu_2$-$\text{O}^2$ (e. g. O4), $\mu_2$-$\text{O}^2$ (e. g. O1, O2, O3) and $\mu_2$-$\text{O}^2$ (e. g. O5). The entire OEC is embedded in a large protein matrix through H-bond interactions and direct ligations to six carboxylate and one imidazole groups of the amino acid residues on the D$_1$ and CP$_{43}$ polypeptides in PSII. Ca$^{2+}$ is known as an essential component for the function of OEC$^{6, 7}$, which can be functionally replaced only by Sr$^{2+}$ without significant disturbing the structure of OEC$^{8, 9}$.

![Fig. 1 Scheme for the OEC in PSII](image)

The water-splitting reaction involves five different S-states ($S_n$, n = 0 ~ 4) of the OEC. Spectroscopic studies have shown that the oxidation states and the geometry of the OEC undergo changes during these state transitions$^{8, 9}$. However, the detailed catalytic mechanism of the OEC, including the role of Ca$^{2+}$/Sr$^{2+}$ in PSII remains under extensive debate$^{10-14}$. Due to the structural complexity of the OEC, it is of a great challenge for chemists to synthesize accurate structural and functional models for the OEC in laboratory.

![Fig. 2 The structure of complex 1. Mn, Sr, O, N, C and H are shown in yellow, violet, red, blue, cyan and green, respectively. For clarity, all hydrogen atoms except two active protons of pivalic acids are omitted. H-bonds are shown with dashed line, and values display the H-bond lengths.](image)
The lengths of the two $\mu_2$-O$^2-$Mn in the complex 1 are in the range of 1.84 Å to 1.87 Å with an average of 1.86 Å, which is a common distance for $\mu_2$-O$^2-$Mn in most multinuclear Mn complexes and heteronuclear MnSr or MnCa complexes$^{24,25,35,39}$. However, the length of 1.86 Å is remarkable shorter (by 0.64 Å) than the average value of 2.5 Å in the OEC of Ca$^{2+}$ or Sr$^{2+}$ containing PSII$^{5}$. It is important to point out that the $\mu_2$-O$^2-$ atom in the OEC has attracted extensive attentions in the studies of water oxidation in PSII recently$^{16,17,40}$. Theoretical studies$^{16,17}$ have suggested that the $\mu_2$-O$^2-$ atom may act as one source of oxygen atom for the formation of O-O bond in the higher S-state (e.g. S$_3$, S$_4$) of the OEC, in which the valences for all Mn ions are most likely to be +4$^{3,9}$, similar to that in complex 1. It is noticed that the assignment of this $\mu_2$-O$^2-$ atom was suffered by its weak electron density compared to all other bridging oxido moieties in the OEC in the X-ray diffraction data$^{4,5,39}$. The structural characteristics of the $\mu_2$-O$^2-$ in complex 1 and various MnSr/MnCa complexes$^{24,25,35}$ could be considered as structural evidences to argue that the binding and the function of the $\mu_2$-O$^2-$ atom in the OEC is worth being addressed in future.

EPR measurements of complex 1 display a similar EPR signals as observed in Mn$_2$Ca$_2$O$_4$ complex reported by Christou’s group$^{35}$. It was found that both solid and solution samples of complex 1 give rise to similar EPR signals (Fig. S5), which suggests that the entire structure of complex 1 is maintained not only in crystal but also in solution.

Cyclic voltammograms (CV) measurements (Fig. 4) of complex 1 display two irreversible redox processes at $-0.5$ V and $+0.9$ V vs. NHE, assigned to the couples of [Mn$^{II}$]Mn$^{IV}$SrO$_4$/[Mn$^{IV}$]$_2$SrO$_4$] and [Mn$^{IV}$]$_3$SrO$_4$]_[Mn$^{III}$]Mn$^{IV}$SrO$_4$]], respectively, according to previous report$^{34,44}$. The irreversibility of these two couples may reflect some structural changes during the redox processes. It is noticed that the $+0.9$ V redox process appears only after undertaking the $-0.5$ V irreversible redox process (Fig. S6 and Fig. S7), suggesting that the occurrence of the former requires the structural change taking place during the redox process of the latter. Interestingly, the $+0.9$ V redox potential was not observed in previous Mn$^{IV}$CaO$_4$ or Mn$^{IV}$SrO$_4$ complexes$^{34,36}$, while it is close to the $+0.8$ V vs. NHE redox potential$^{37,38}$ of the OEC in PSII.

In summary, a new complex is synthesized with remarkable
structural similarities to the OEC in $\text{Sr}^{2+}$-containing PSII, in respects of the peripheral ligands, the $\text{Mn}_5\text{Sr}_4\text{O}_7$ cuboidal moiety, and the three different types of bridging oxido moieties at the same time. The redox characteristics of this new complex are close to that of the OEC, as well. Therefore, the complex 1 may serve as a highly accurate synthetic model of the OEC in PSII, which may provide new insights into the understanding of the structure and properties of the OEC in nature.

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Notes and references

# Polymer Materials Research Center, Key Laboratory of Superlight Materials & Surface Technology, Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China. E-mail: dhongxing@hrbeu.edu.cn; Tel: 86-451-82568191;
# Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: chunchizhang@iccas.ac.cn; Fax: 86-10-82671751; Tel: 86-10-82671703;
† Electronic Supplementary Information (ESI) available: Experimental section, X-ray structure information, BVS calculations, UV-vis absorption spectrum, EPR spectrum, Cyclic voltammogram (CV), Differential pulse voltammogram (DPV). See DOI: 10.1039/b000000x/c;
‡ Elemental analysis (%) calcld. for complex 1 (C$_{30}$H$_{36}$N$_2$O$_{28}$Mn$_4$Sr): C, 41.57; H, 5.98; N, 1.38; found: C, 41.57; H, 5.79; N, 1.63; Crystal structure data for complex 1: C$_{30}$H$_{36}$N$_2$O$_{28}$Mn$_4$Sr; $M = 2022.56$, black rod crystal, orthorhombic, $P2_12_12_1$, $a = 15.290(3)$, $b = 18.205(4)$, $c = 36.041(7)$ Å, $a = 90.00$, $\beta = 90.00$, $\gamma = 90.00^\circ$, $V = 10032(3)$ Å$^3$, $32066$ reflections collected; $1083$ parameters were refined in the final cycle of refinement using 17540 reflections (I $> 2\sigma$(I)); $R1 = 0.0947$, $wR2 = 0.2202$ (based on $F^2$ and all data). Also see CCDC 994140 for complex 1.