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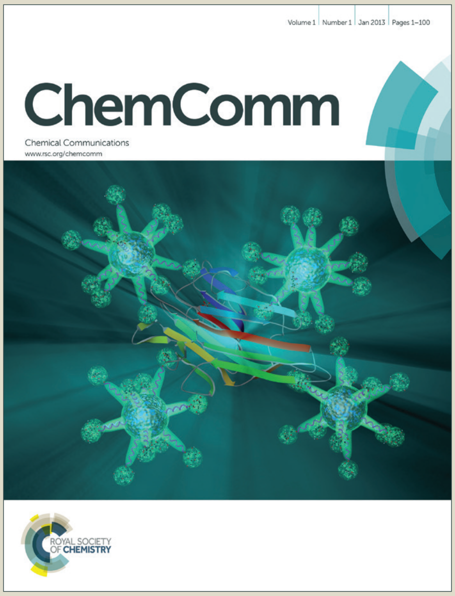

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ARTICLE TYPE

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

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A novel heterometallic MnSr complex containing Mn_3SrO_4 cuboidal moiety and all types of μ-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, 2]. The structure of OEC has been recently revealed by X-ray crystal structure of PSII (**Fig. 1**)[3-5]. There are two unique characteristics in the structural motif of OEC. One is the incorporation of Ca^{2+} within the Mn_3CaO_4 cubane through three μ-oxido moieties. The other is the simultaneous presence of μ_2-O^{2-} (*e. g.* O4), μ_3-O^{2-} (*e. g.* O1, O2, O3) and μ_4-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], which can be functionally replaced only by Sr^{2+} without significant disturbing the structure of OEC[5, 7]

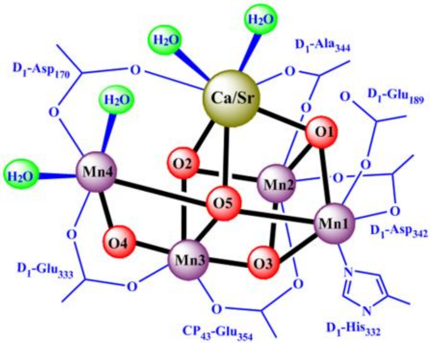

Fig. 1 Scheme for the OEC in PSII

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[10-17]. 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.

To date, many multinuclear Mn complexes have been synthesized as models of the OEC[1, 18-23]. In contrast only a few synthetic MnCa and MnSr heterometallic complexes[24-36] have been reported. Moreover, no effort has been made to mimic the three types of bridging oxido moieties (μ_2-O^{2-}, μ_3-O^{2-} and μ_4-O^{2-}) at the same time. In terms of the functional properties, the redox potentials of current two complexes containing $Mn^{IV}_3CaO_4$ or $Mn^{IV}_3SrO_4$ cuboidal moieties with a multinucleating ligand [34, 36] were very low, -0.5V vs NHE, comparing to the requirement for the thermodynamic potential for water oxidation (+0.8V vs NHE)[37, 38]. Therefore, it is highly desirable to synthesize more accurate structural and functional models for the OEC.

Here, we report a novel MnSr complex contains Mn_3SrO_4 cuboidal moiety and all types of μ-oxido moieties observed in the OEC, in addition, it exhibits the redox potential at + 0.9 V vs NHE, suggesting its potential as a good synthetic model for the OEC.

This complex was synthesized in a reaction of $Bu^n_4NMnO_4$, $Mn(CH_3CO_2)_2(H_2O)_4$ and $Sr(CH_3CO_2)_2(H_2O)_{0.5}$ with a molar ratio of 4 : 1 : 1 in boiling acetonitrile with the presence of an excess of pivalic acid. Red-brown crystal was formed after cooling, which was further recrystallized in ethyl acetate solution with the presence of ~ 2% pyridine (details of preparation, see **ESI**). Final product of complex **1,** $[Mn^{IV}_6Sr_2O_9(Bu^tCO_2)_{10}(Bu^tCO_2H)_2(C_5H_5N)_2]$ was obtained in black rod crystal with a yield of 22% (on Strontium basis).

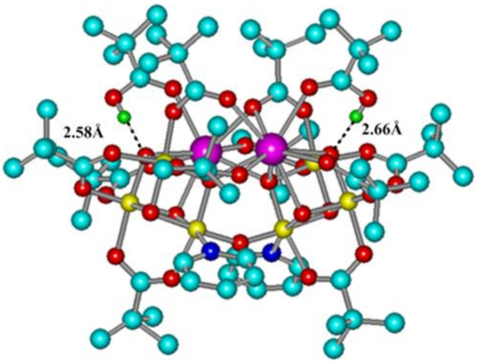

Fig. 2 The structure of complex **1**. Mn, Sr, O, N, C and H are shown in yellow, violet, red, blue, cyan and green, respectively. For clarity, all hydrogen atoms except two active protons of pivalic acids are omitted. H-bonds are shown with dashed line, and values display the H-bond lengths.

Fig. 2 shows the crystal structure of complex **1**. The peripheral ligands of complex **1** include ten pivalate, two pivalic acid and two pyridine groups. Each coordinated pivalic acid further interacts with μ_3-O^{2-} through a strong H-bond (**Fig. S2**). All these ligations and H-bond interactions in complex **1** are reminiscent of the protein environment of the OEC in PSII[3-5].

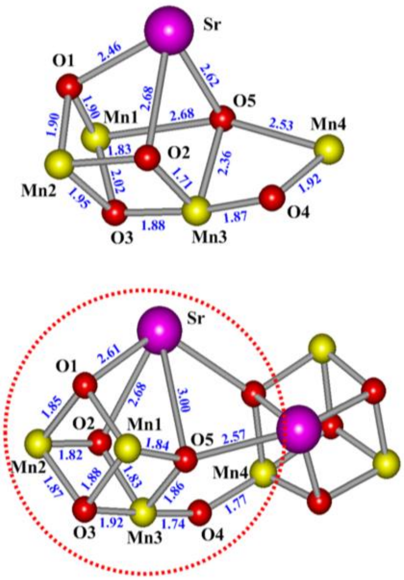

Fig. 3 The core of complex **1** (bottom) and OEC in PSII (top). The fraction of Mn_4SrO_5 of complex **1** similar to the OEC is emphasized with a red-dashed circle. The values display the lengths of selected bonds (Å).

All six Mn ions are six-coordinate. The two Sr^{2+} ions are eight- and nine-coordinate, respectively, resulting in the asymmetry of the entire structure of complex **1** (**Table S3).**

In the core of complex **1,** two $Mn^{IV}_3SrO_4$ cuboidal units are connected by one μ_2-O^{2-} and two μ_4-O^{2-} moieties. Three types of μ-O^{2-} moieties (μ_2-O^{2-},μ_3-O^{2-}, μ_4-O^{2-}) are seen in complex **1**. The +4 valence of all six Mn ions and the doubly deprotonated state of all bridged oxygen atoms are confirmed by bond-valance sum calculations (**Table S4**). To our knowledge, this is the first time to synthesize a MnSr complex containing three types of μ-O^{2-} moieties simultaneously. Therefore, complex **1** provides an artificial model to interrogate the functionalities of these μ-O^{2-} moieties in the OEC of PSII.

The average distances of Mn-Sr in complex **1** is 3.58 Å, which is longer than 3.40 Å in previous Mn_3SrO_4 complex containing a multinucleating ligand[34], but is close to the 3.55 Å separation observed in OEC of Sr^{2+}-containing PSII[5] (**Table S5**). The average 2.77 Å distances of Mn-Mn in complex **1** is slight shorter than that observed previously in Mn_3SrO_4 complex[34] (2.82 Å), and also obviously shorter than 3.00 Å for that in the OEC of Sr^{2+}-containing PSII[5], it is likely because of the higher oxidation states of the Mn ions in complex **1**.

The average distance of μ_3-O–Mn in the complex **1** is 1.86 Å, which is slight shorter than 1.88 Å observed in the OEC of Sr^{2+}-containing PSII[5], or 1.87 Å in Mn_3SrO_4 complex reported[34]. The average distance of μ_2-O–Mn in the complex **1** is 1.76 Å, which is shorter than 1.89 Å observed in OEC of Sr^{2+}-containing PSII[5] (**Table S5**), it is likely because of the higher oxidation state of the Mn ions in complex **1**, as well.

The lengths of the two μ_4-O–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 μ_4-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[4, 5]. It is important to point out that the μ_4-O5 atom in the OEC has attracted extensive attentions in the studies of water oxidation in PSII recently[14, 16, 17, 39-43]. Theoretical studies[16, 17] have suggested that the μ_4-O5 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[8, 9], similar to that in complex **1**. It is noticed that the assignment of this μ_4-O5 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 μ_4-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 μ_4-O5 atom in the OEC is worth being addressed in future.

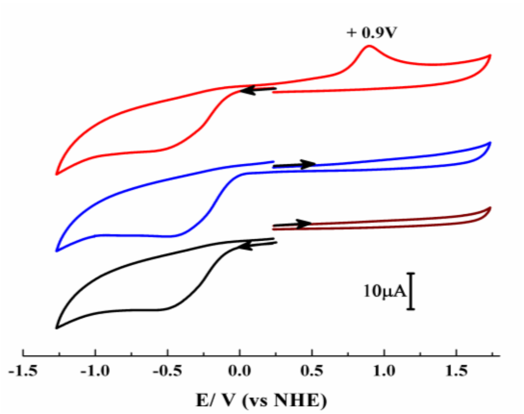

Fig. 4 Cyclic voltammogram of complex **1** in 3:2 ratio of $EtCl_2$/ethyl acetate. Potentials are referenced to NHE. Scan rate: 100mV/s, Arrows display the scan direction.

EPR measurements of complex **1** display a similar EPR signals as observed in $Mn_3Ca_2O_4$ 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 $[Mn^{III}Mn^{IV}_2SrO_4]$ /$[Mn^{IV}_3SrO_4]$ and $[Mn^{IV}_3SrO_4]$/$[Mn^{V}Mn^{IV}_2SrO_4]$, 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 $Mn^{IV}_3CaO_4$ or $Mn^{IV}_3SrO_4$ complexes [34, 36], while it is close to the + 0.8 V~ +0.9 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 Sr^{2+}-containing PSII, in respects of the peripheral ligands, the Mn_3SrO_4 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

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‡ Elemental analysis (%) calcd. for complex **1** ($C_{70}H_{120}N_2O_{33}Mn_6Sr_2$): 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**: $C_{70}H_{120}N_2O_{33}Mn_6Sr_2$, $M = 2022.56$, black rod crystal, orthorhombic, $P2_12_12_1$, $a = 15.290(3)$, $b = 18.205(4)$, $c = 36.041(7)$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 90.00°$, $V = 10032(3)$ 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**.

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