

Supporting Information to the paper entitled:

**Trigonal Propeller-shaped  $\text{Mn}^{\text{III}}_3\text{M}^{\text{II}}\text{Na}$  Complexes (M = Mn, Ca):  
Structural and Functional Models for the Dioxygen Evolving Centre  
of PSII**

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**List of contents:**

Table S1: Relevant M-M and M-L distances in compounds **1** and **2**.

Table S2: List of bond lengths in compound **1**.

Table S3: List of important bond angles in compound **1**.

Table S4: List of bond lengths in compound **2**.

Table S5: List of important bond angles in compound **2**.

Figure S1. The cyclic voltammetry plot for compound **2**.

Figure S2. Detection of  $^{18}\text{O}$  during dioxygen evolution study using labeled isotope of water using online mass spectroscopy.

Figure S3. Illustration of the spin density.

**Table S1:** Relevant M-M and M-L distances in compounds **1** and **2** (in Å)

<i>Compound 1</i>	Mn <sup>III</sup> -Mn <sup>II</sup>	3.56-3.60	Mn <sup>III</sup> -Na	3.25-3.31	Mn <sup>II</sup> -O	2.08-2.22
	Mn <sup>III</sup> -O(oxide)	1.89-1.90	Mn <sup>III</sup> -Cl	2.45-2.69	Mn <sup>III</sup> -Mn <sup>III</sup>	3.23-3.26
	Mn <sup>III</sup> -N	1.97-1.98	Na-Cl	2.67	Na-O	2.39-2.41
<i>Compound 2</i>	Mn <sup>III</sup> -Ca	3.44-3.48	Mn <sup>III</sup> -Na	3.75-3.80	Ca-O	2.36-2.46
	Mn <sup>III</sup> -O(oxide)	1.88-1.90	Mn <sup>III</sup> -N(azide)	2.27-2.36	Mn <sup>III</sup> -Mn <sup>III</sup>	3.10-3.11
	Mn <sup>III</sup> -N	1.98-1.99	Mn-O	1.90-1.91	Na-O	2.35-2.40

**Table S2:** List of bond lengths in compound 1.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance (Å)
Mn1	Cl2	2.6672(9)	C6	C124	1.417(6)
Mn1	Cl4	2.599(1)	C7	C16	1.419(5)
Mn1	O12	1.900(2)	C7	H7	0.91(4)
Mn1	O1	1.899(2)	C8	C18	1.420(5)
Mn1	O4	1.893(3)	C8	C35	1.439(5)
Mn1	N8	1.975(3)	C9	H9	1.10(4)
Mn2	Cl4	2.689(1)	C10	H10	1.000(5)
Mn2	O1	1.904(2)	C10	C23	1.465(7)
Mn2	O2	1.884(2)	C10	C27	1.506(6)
Mn2	O3	1.910(2)	C11	H11	0.949(4)
Mn2	N2	1.975(3)	C11	C16	1.409(4)
Mn2	Cl7	2.453(2)	C11	C21	1.370(6)
Mn4	O22	2.112(3)	C12	H12	0.950(4)
Mn4	O2	2.136(2)	C12	C121	1.387(5)
Mn4	O4	2.086(3)	C12	C122	1.390(5)
Mn4	O5	2.215(3)	C13	C16	1.416(5)
Mn4	O6	2.204(3)	C13	C20	1.379(6)
Mn4	O9	2.223(3)	C14	H14	0.950(4)
Mn3	Cl2	2.582(1)	C14	C18	1.357(6)
Mn3	O11	1.914(2)	C14	C19	1.388(6)
Mn3	O1	1.896(2)	C18	H18	0.951(3)
Mn3	O22	1.883(3)	C19	H19	0.950(4)
Mn3	N7	1.986(3)	C20	H20	0.951(4)
Mn3	Cl7	2.635(2)	C20	C22	1.402(5)
Cl3	Na5	2.671(2)	C21	H21	0.950(3)
O11	C35	1.322(4)	C21	C22	1.388(6)
O11	Na5	2.415(2)	C22	H22	0.950(5)
O12	Na5	2.348(3)	C23	H23A	0.990(6)
O12	C121	1.333(4)	C23	H23B	0.989(4)
O1	Na5	2.401(2)	C26	H26A	0.991(4)
O2	C10	1.423(4)	C26	C28	1.395(8)
O3	C13	1.325(3)	C27	H27A	0.989(4)
O3	Na5	2.390(3)	C27	H27B	0.990(6)
O4	C234	1.474(6)	C28	C29	1.402(7)
N2	C7	1.280(4)	C29	H29A	0.990(6)
N2	C27	1.476(6)	C29	H29B	0.990(4)
N7	C45	1.287(5)	C122	H122	0.951(4)
N7	C26	1.466(5)	C122	C123	1.394(6)
O5	C23	1.434(5)	C124	H124	0.949(4)
N8	C9	1.286(5)	C111	C234	1.634(8)

N8	C111	1.465(5)	C234	H234	0.999(5)
O9	C236	1.375(8)	C236	H23D	0.991(6)
C6	C9	1.426(5)	OW3	CW3	1.28(2)
C6	C121	1.415(4)	OW2	CW2	1.52(3)

**Table S3:** List of important bond angles in compound 1.

Atom 1	Atom 2	Atom 3	Angle 1-2-3	Atom 1	Atom 2	Atom 3	Angle 1-2-3
Mn1	Cl2	Mn3	76.12(3)	Mn2	O1	Na5	98.62(9)
Mn1	Cl4	Mn2	76.13(3)	Mn3	O1	Na5	100.39(9)
Mn3	O11	Na5	99.36(9)	Mn4	O22	Mn3	126.0(1)
C35	O11	Na5	130.5(2)	Mn2	O2	Mn4	127.1(1)
Mn1	O12	Na5	99.6(1)	Mn2	O3	Na5	98.84(9)
Mn1	O1	Mn2	118.1(1)	C13	O3	Na5	128.8(2)
Mn1	O1	Mn3	117.1(1)	Mn1	O4	Mn4	127.0(2)

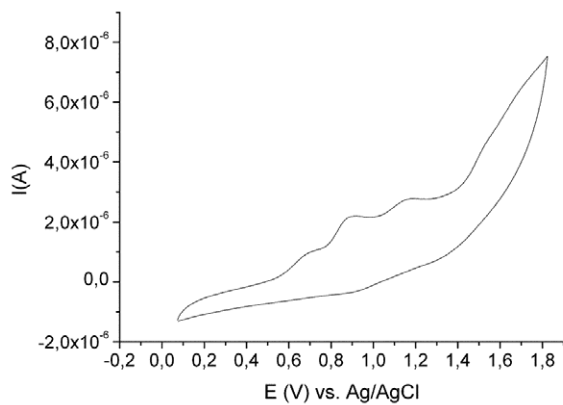
**Table S4:** List of bond lengths in compound 2.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance (Å)
Mn1	Mn3	3.112(1)	Mn3	N3	1.976(6)
Mn1	O2	1.899(4)	Mn3	N14	2.268(5)
Mn1	O3	1.881(4)	Mn3	N17	2.304(5)
Mn1	O20	1.900(4)	Ca4	O3	2.335(5)
Mn1	N1	1.982(5)	Ca4	O4	2.407(6)
Mn1	N11	2.362(6)	Ca4	O7	2.363(4)
Mn1	N17	2.324(5)	Ca4	O8	2.445(7)
Mn2	Mn3	3.101(1)	Ca4	O11	2.354(4)
Mn2	O6	1.908(4)	Ca4	O12	2.439(8)
Mn2	O7	1.885(4)	Ca4	O22	2.462(6)
Mn2	O20	1.898(4)	Na1	O1	2.478(5)
Mn2	N2	1.983(5)	Na1	O2	2.357(4)
Mn2	N13	2.339(5)	Na1	O5	2.460(4)
Mn2	N14	2.333(5)	Na1	O6	2.341(5)
Mn3	O10	1.914(4)	Na1	O9	2.421(4)
Mn3	O11	1.887(4)	Na1	O10	2.340(5)
Mn3	O20	1.928(4)	Na1	O20	2.759(4)

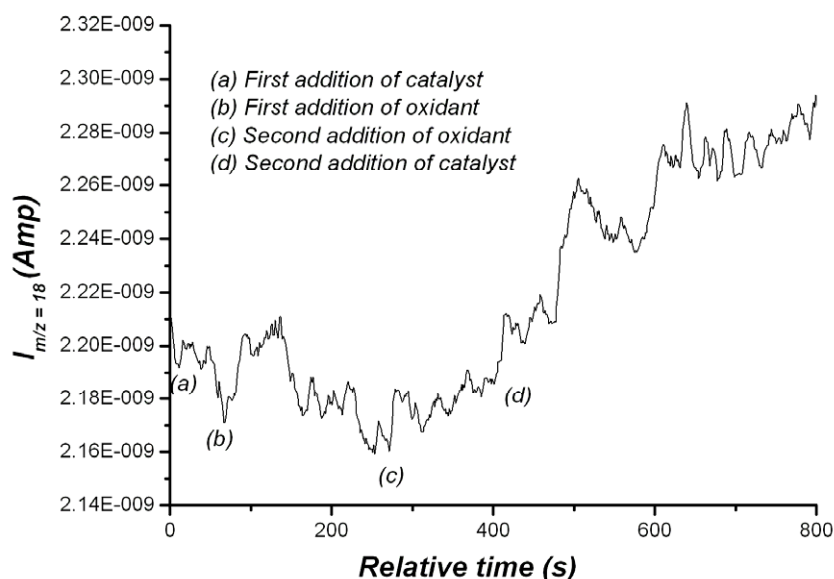
**Table S5:** List of important bond angles in compound 2.

Atom 1	Atom 2	Atom 3	Angle 1-2-3	Atom 1	Atom 2	Atom 3	Angle 1-2-3
Mn1	O2	Na1	109.5(2)	Mn1	O20	Mn3	108.8(2)
Mn1	O3	Ca4	125.2(2)	Mn1	O20	Na1	95.0(2)
Mn2	O6	Na1	107.7(2)	Mn2	O20	Mn3	108.2(2)
Mn2	O7	Ca4	126.6(2)	Mn2	O20	Na1	93.4(2)

Mn3	O10	Na1	108.0(2)	Mn3	O20	Na1	93.1(1)
Mn3	O11	Ca4	124.7(2)	Mn2	N14	Mn3	84.7(2)
Mn1	O20	Mn2	141.5(2)	Mn1	N17	Mn3	84.5(2)



**Figure S1.** The cyclic voltammety plot for compound **2** against Ag/AgCl electrode in acetonitrile is shown.



**Figure S2.** Detection of  $^{18}\text{O}$  during dioxygen evolution study using labeled isotope of water using online mass spectroscopy.

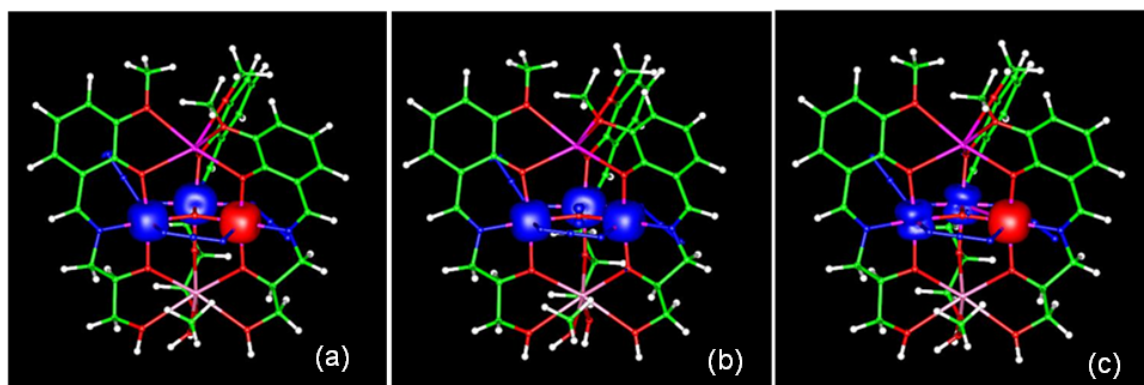
### Computational Studies:

In order to gain further insight in the electronic situation of both the  $[\text{Mn}^{\text{III}}_3\text{Ca}^{\text{II}}\text{Na}^{\text{I}}]$  and the  $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{IV}}\text{Ca}^{\text{II}}\text{Na}^{\text{I}}]$  system, density functional theory (DFT)<sup>1,2</sup> calculations of the cation in **2** were performed by employing the program system TURBOMOLE.<sup>3,4</sup> The simultaneous simulations of the electronic and geometric structure of the complex were based on the X-ray structural parameters.<sup>5-10</sup>

These studies revealed that the mono-cation of **2** is very likely to adopt an intermediate  $S = 4/2$  ground state, being energetically advantaged over the high spin  $S = 12/2$  state by  $10.7 \text{ kJ}\cdot\text{mol}^{-1}$ , which is again lower in energy than the low spin  $S = 0$  state by  $9.3 \text{ kJ}\cdot\text{mol}^{-1}$ . This was also evidenced from the experimental finding of the magnetization measurement of this compound (see SI for details) and compounds with a quite similar core.<sup>11</sup> In the  $S = 4/2$  state, the three  $d^4$  high-spin  $\text{Mn}^{3+}$  ions show magnetic frustration by two antiferromagnetic interactions and one ferromagnetic interaction along the  $\text{Mn}_3$  triangle. Other than may be expected, the magnetic interaction does not resemble the structural diversity in the  $\text{Mn}_3$  triangle: the only edge to be bridged by a  $\mu(\text{N}_3\text{-N}^1, \text{N}^3)^-$  ligand represents one of the antiferromagnetic edges, whereas the only ferromagnetic coupling arises along one of the two  $\mu(\text{N}_3\text{-N}^1, \text{N}^1)^-$  bridged edges. In the

ferromagnetic  $S = 12/2$  state all Mn ions have the same spin state and orientation and the  $S = 0$  state is realized by an alpha and beta spin distribution similar to the ground state  $S = 4/2$  situation, but with two Mn ions in intermediate  $s = 2/2$  spin states.

In Figure 6, the spin densities in these three cases are illustrated. In order to elucidate the most probable site of oxidation within a catalytic process, a vertical detachment of an electron has been calculated for the optimized ground state species with  $S = 4/2$ . As could be expected for the ionization of a cation, the di-cation is 0.72 eV higher in energy than the ground state. However, the natural bond orbital (NBO) analyses revealed that during the oxidation, most of the charge density is withdrawn from the O and N donor ligands, whereas the Mn atoms remain nearly unchanged in charge density.



**Figure S3.** Illustration of the spin density (i.e. differences of the electron densities of  $\alpha$  (blue) and  $\beta$ -spins (red) for each atom, drawn to  $0.2 \text{ e}^- \cdot \text{\AA}^{-3}$ ), in the mono-cation in **2** at its  $S = 4/2$  ground state (a) and the  $S = 12/2$  (b) and  $S = 0$  (c) excited states. The pictures were generated using the program gOpenMol.<sup>12</sup>

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Supplementary Material (ESI) for Dalton Transactions

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