A series of new structural models for the OEC in photosystem II

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Bond Valence Sum Calculations for Compounds **1**, **2** and **3**

Compound	**1**		**2**		**3**	
	$r_o(Mn^{III})$	$r_o(Mn^{II})$	$r_o(Mn^{III})$	$r_o(Mn^{II})$	$r_o(Mn^{III})$	$r_o(Mn^{II})$
Mn(1)	**3.20**	3.53	**3.13**	3.37	**3.08**	3.31
Mn(2)	**3.10**	3.27	**3.18**	3.40	**3.06**	3.29
Mn(3)	**3.13**	3.36	**3.19**	3.37	**3.19**	3.43
Mn(4)	1.76	**1.87**	1.81	**1.96**	**3.03**	3.26
O(1)	**-1.99**		**-2.02**		**-2.06**	

For each Mn centre, the oxidation states were calculated twice, using the r_o values for Mn^{III} followed by those for Mn^{II}. The values in bold are those for which the calculated and input oxidation states are in good agreement. These oxidation states were then used to calculate the charge on O(1) for each complex, confirming the assignments (based on their coordination to four metal centres with a tetrahedral geometry) as $(\mu_3\text{-}O)^{2-}$ rather than hydroxo ligands. In addition, the bond lengths around the Mn centres are reasonable for these assignments and the Mn(III) ions show the expected Jahn-Teller distortions for high spin d^4 ions.

References:

W. Liu and H. H. Thorp, *Inorg. Chem.*, 1993, *32*, 4102-4105.

N. E. Brese and M. O'Keefe, *Acta Cryst.*, 1991, *B47*, 192-197.

Synthetic procedures:

1: The Schiff-base was made *in situ* in a methanolic solution (20 mL) of *o*-vanillin (1.0 mmol, 0.152 g), 1-amino-2-propanol, (1.0 mmol, 0.075 g), triethylamine (1.0 mmol, 0.101 g) and $CaCl_2$ (2.0 mmol, 0.222 g) which was added to a second methanolic solution (20 mL) of $Mn(OAc)_2•4H_2O$ (1.0 mmol, 0.245 g) with stirring at room temperature. Greenish-brown crystalline needles were deposited after 1 day; yield 63 mg (19%). Found (%): C, 37.1; H, 5.2; N, 4.1. Calc. (%) for $C_{35.7}H_{46.8}CaCl_{3.8}Mn_4N_3O_{14.2}$ (corresponds to loss of lattice solvent): C, 37.62; H, 4.14; N, 3.69. IR (KBr disc): 3400 (br), 1638 (s), 1453 (m), 1223 (m), 1043 (m), 743 (w).

2: Procedure as for **1** except with NaN_3 (2.0 mmol, 0.130 g) in place of $CaCl_2$. Brown crystalline needles were deposited after 1 week; yield 220 mg (75%). Found (%) C 36.6; H 4.5; N 12.8. Calc. (%) for $C_{36.6}H_{58.9}Mn_4NaN_{11.1}O_{19.6}$ (corresponds to $\{Mn_4Na\}·6H_2O$): C 36.31; H 4.90; N 12.84. IR (KBr disc): 3400 (br), 2042 (s), 1634 (s), 1443 (m), 1221 (m), 1041 (m), 745 (w).

3: The Schiff-base was made *in situ* in a methanolic solution (20 mL) of *o*-vanillin (1.0 mmol, 0.152 g), 2-amino-1,3-propanediol, (1.0 mmol, 0.091 g), triethylamine (1.0 mmol, 0.101 g) and NaN_3 (2.0 mmol, 0.130 g) which was added to a second methanolic solution (20 mL) of $MnCl_2•4H_2O$ (1.0 mmol, 0.198 g) with stirring at room temperature. Brown crystalline blocks were deposited after 2 days; yield 310 mg (46%). Found (%) C 37.3; H 4.6; N 11.4. Calc. (%) for $C_{90}H_{150}CaClMn_8N_{23}O_{51}$ (corresponds to $\{Na_2Mn_8\}Cl•15H_2O$): C 37.39; H 5.23; N 11.14. IR (KBr disc): 3370 (m), 2053 (s), 1619 (s), 1439 (m), 1249 (m), 1050 (w), 740 (m).

Magnetic measurements:

Data were measured on a SQUID MPMS-X7 susceptometer using 9.6 mg of **1**, 11.6 mg of **2** and 12.9 mg of **3** in the temperature range 1.8 to 300 K with a 1000 Oe applied field.