Tetranuclear Manganese Cluster Complexes Obtained by Ligand Substitution Reactions

Christopher E. Dubé[1], Sumitra Mukhopadhyay[1], Peter J. Bonitatebus, Jr.[1], Richard J. Staples[2], and William H. Armstrong[1]

[1]*Department of Chemistry, Boston College,* [2]*Department of Chemistry and Chemical Biology, Harvard University*

A series of adamantane-shaped $[Mn_4O_6]^{4+}$ aggregates has been prepared. Ligand substitution reactions of $[Mn_4O_6(bpea)_4](ClO_4)_4$ (**1**) with tridentate amine and iminodicarboxylate ligands (R-ida) in acetonitrile affords derivative clusters $[Mn_4O_6(tacn)_4](ClO_4)_4$ (**4**), $[Mn_4O_6(bpea)_2(dien)_2](ClO_4)_4$ (**5**), $[Mn_4O_6(Medien)_4](ClO_4)_4$ (**6**), $[Mn_4O_6(tach)_4](ClO_4)_4$ (**7**), $[Mn_4O_6(bpea)_2(me\text{-}ida)_2]$ (**8**), $[Mn_4O_6(bpea)_2(bz\text{-}ida)_2]$ (**9**), $[Mn_4O_6(bpea)_2(^t bu\text{-}ida)_2]$ (**10**) and $[Mn_4O_6(bpea)_2(^c pent\text{-}ida)_2]$ (**11**) generally on the order of 10 minutes at room temperature with retention of core nuclearity and oxidation state. Of these complexes, only **4** had been synthesized previously. Characterization of two members of this series by X-ray crystallography reveals that compound **7** crystallizes as $[Mn_4O_6(tach)_4](ClO_4)_4 \cdot 3CH_3CN \cdot 4.5H_2O$ in the cubic space group Fm-3m and compound **11** crystallizes as $[Mn_4O_6(bpea)_2(^c pent\text{-}ida)_2] \cdot 7MeOH$ in the monoclinic space group C2/c. The unique substitution chemistry of **1** with iminodicarboxylate ligands afforded asymmetrically ligated complexes **8**-**11**, the mixed ligand nature of which is most likely unachievable using self-assembly synthetic methods. A special feature of the iminodicarboxylate ligand complexes **8**-**11** is the substantial site differentiation of the oxo bridges of the $[Mn_4O_6]^{4+}$ cores. While there are four site-differentiated oxo bridges in **8**, solution structural symmetry of $\mathbf{8}H^+$ reveals essentially a single protonation isomer, in contrast to the observation of two protonation isomers for $\mathbf{1}H^+$, one for each of its site-differentiated oxo bridges. Magnetic susceptibility measurements on **4**, **7**, **8** and **9** indicate that each complex is overall ferromagnetically coupled and variable-field magnetization data for **7** and **9** are consistent with an S = 6 ground state. Electrochemical analysis demonstrates that ligand substitution of bpea affords accessibility to the $Mn^V(Mn^{IV})_3$ oxidation state. This latter result is of particular interest as several proposed mechanisms for photosynthetic water oxidation hinge on the intermediacy of a Mn(V) species.