Tetranuclear Manganese Cluster Complexes Obtained by Ligand Substitution Reactions

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A series of adamantane-shaped [Mn₄O₆]⁴⁺ aggregates has been prepared. Ligand substitution reactions of [Mn₄O₆(bpea)₄](ClO₄)₄ (1) with tridentate amine and iminodicarboxylate ligands (R-ida) in acetonitrile affords derivative clusters [Mn₄O₆(tacn)₄](ClO₄)₄ (4), [Mn₄O₆(bpea)₂(dien)₂](ClO₄)₄ (5), [Mn₄O₆(Medien)₄](ClO₄)₄ (6), [Mn₄O₆(tach)₄](ClO₄)₄ (7), [Mn₄O₆(bpea)₂(me-ida)₂] (8), [Mn₄O₆(bpea)₂(bz-ida)₂] (9), [Mn₄O₆(bpea)₂(‘bu-ida)₂] (10) and [Mn₄O₆(bpea)₂(‘pent-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 [Mn₄O₆(tach)₄](ClO₄)₄·3CH₃CN·4.5H₂O in the cubic space group Fm-3m and compound 11 crystallizes as [Mn₄O₆(bpea)₂(‘pent-ida)₂]·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 [Mn₄O₆]⁴⁺ cores. While there are four site-differentiated oxo bridges in 8, solution structural symmetry of 8H⁺ reveals essentially a single protonation isomer, in contrast to the observation of two protonation isomers for 1H⁺, 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 Mn⁵(Mn⁴)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.