

Tuning Tetranuclear Manganese–Oxo Core Electronic Properties: Adamantane-Shaped Complexes Synthesized by Ligand Exchange

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A series of adamantane-shaped $[\text{Mn}_4\text{O}_6]^{4+}$ aggregates has been prepared. Ligand substitution reactions of $[\text{Mn}_4\text{O}_6(\text{bpea})_4](\text{ClO}_4)_4$ (**1**) with tridentate amine and iminodicarboxylate ligands in acetonitrile affords derivative clusters $[\text{Mn}_4\text{O}_6(\text{tacn})_4](\text{ClO}_4)_4$ (**4**), $[\text{Mn}_4\text{O}_6(\text{bpea})_2(\text{dien})_2](\text{ClO}_4)_4$ (**5**), $[\text{Mn}_4\text{O}_6(\text{Medien})_4](\text{ClO}_4)_4$ (**6**), $[\text{Mn}_4\text{O}_6(\text{tach})_4](\text{ClO}_4)_4$ (**7**), $[\text{Mn}_4\text{O}_6(\text{bpea})_2(\text{me-ida})_2]$ (**8**), $[\text{Mn}_4\text{O}_6(\text{bpea})_2(\text{bz-ida})_2]$ (**9**), $[\text{Mn}_4\text{O}_6(\text{bpea})_2(\text{bu-ida})_2]$ (**10**), and $[\text{Mn}_4\text{O}_6(\text{bpea})_2(\text{pent-ida})_2]$ (**11**) generally on the order of 10 min 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 $[\text{Mn}_4\text{O}_6(\text{tach})_4](\text{ClO}_4)_4 \cdot 3\text{CH}_3\text{CN} \cdot 4.5\text{H}_2\text{O}$ in the cubic space group $Fm\bar{3}m$ and compound **11** crystallizes as $[\text{Mn}_4\text{O}_6(\text{bpea})_2(\text{pent-ida})_2] \cdot 7\text{MeOH}$ 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 $[\text{Mn}_4\text{O}_6]^{4+}$ cores. While there are four site-differentiated oxo bridges in **8**, the 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 the site-differentiated oxo bridges in **1**. 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 $\text{Mn}^{\text{V}}(\text{Mn}^{\text{IV}})_3$ oxidation state.

Introduction

The molecular oxygen essential to life on earth is produced by the light-driven catalytic oxidation of water by photosystem II (PSII). Simultaneously, the oxygen-evolving complex (OEC) of PSII supplies the reducing equivalents employed by PSI in providing most of life's chemical energy. The OEC stores oxidizing equivalents in a series of steps (S-states) known as the Kok cycle, culminating in the oxidation of water and the release of O_2 . Key components

of the OEC include a compact, magnetically coupled tetranuclear manganese–oxo complex, Ca^{2+} and Cl^- cofactors, and a redox-active tyrosine residue, Y_z .^{1–6} Despite the host of biophysical methods used to examine the OEC, an accurate model for the active site manganese aggregate has not been forthcoming. X-ray crystal structures of PSII from cyanobacteria *Thermosynechococcus elongatus*⁷ and *Thermosynechococcus vulcanus*⁸ reveal density attributed to the manganese cluster for the first time. Pertinent electron density

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data are consistent with three manganese ions arranged in an approximate isosceles triangle, with a fourth manganese ion located near the center of the triangle. Electron density data for *T. vulcanus* also supports the assignment of the C-terminal carboxyl group of D1 Ala344 as a ligand to the manganese aggregate, as well as a number of other D1 aspartate, glutamate, and histidine residues as additional possible ligands. More recently the structure of PSII from *T. elongatus* identified the electron density attributed to four manganese ions and a fifth metal ion, which was modeled as Ca^{2+} .⁹ Similar to the previous study with *T. elongatus*, several D1 aspartate, glutamate, and histidine residues were proposed as possible ligands for the manganese cluster, as well as a CP43 aspartate, although in the present study the C-terminal carboxyl group of Ala344 is not coordinated to the metal cluster. It should be noted, however, that uncertainties associated with these X-ray structures, as well as possible irradiation effects,¹⁰ make it difficult to assign atom connectivity within the manganese aggregate as well as between the metal cluster and associated peptide residues. $\text{Mn}\cdots\text{Mn}$ distances in these structures are approximately 3 Å. These data are similar to those obtained with extended X-ray absorption fine structure (EXAFS) studies of the S_2 state, which indicate at least two 2.7 Å $\text{Mn}\cdots\text{Mn}$ vectors, as well as a longer 3.3 Å $\text{Mn}\cdots\text{Mn}$ (or $\text{Mn}\cdots\text{Ca}$) vector.^{6,11–14} Although precise details of the ligand environment remain an area of active investigation, it is believed that the Mn complex is coordinated predominantly by oxide and carboxylates (i.e. aspartate and glutamate) and one or two imidazoles.^{8,9,15–17}

Insight into the structure and mechanism of action of the OEC has been achieved through synthesis, characterization, and reactivity studies of high-valent tetranuclear manganese-oxo aggregates, such as the adamantane-shaped $[\text{Mn}_4(\mu\text{-O})_6]^{4+}$,^{18–22} $[\text{Mn}_4(\mu\text{-O})_6]^{3+}$,^{21–24} $[\text{Mn}_4(\mu\text{-O})_5(\text{OH})]^{5+}$,^{20,21} and

$[\text{Mn}_4(\mu\text{-O})_4(\text{OH})_2]^{6+}$,²⁵ open chain $[\text{Mn}_4(\mu\text{-O})_6]^{4+26–28}$ and $[\text{Mn}_4(\mu\text{-O})_6]^{3+}$ cores;²⁹ the cubane-like $[\text{Mn}_4(\mu_3\text{-O})_3(\mu_3\text{-X})]^{4+}$,^{30–33} $[\text{Mn}_4(\mu_3\text{-O})_4]^{6+}$,^{34, 35} and $[\text{Mn}_4(\mu_3\text{-O})_4]^{7+}$,³⁶ the butterfly-shaped $[\text{Mn}_4(\mu_3\text{-O})_2(\mu\text{-OAc})_7]^{+}$,^{37–40} a stacked dimer-of-dimers $[\text{Mn}_2(\mu\text{-O})_2(\mu\text{-OR})_2]^{4+}$,^{41–43} an open dimer-of-dimers $[\text{Mn}_4(\mu\text{-O})_5]^{6+}$,⁴⁴ and an open species $[\text{Mn}_4(\mu\text{-O})_5]^{6+}$.⁴⁵

Consideration of PSII biophysical studies as well as of the coordination chemistry of manganese has led to a number of proposals for the mechanism of photosynthetic O_2 evolution. Of particular note here are EXAFS studies comparing the S_2 and S_3 states. EXAFS data suggest that advancement from S_2 to S_3 is accompanied by structural changes in the PSII Mn_4 complex, although these studies have led to very different conclusions. In one study, these changes have been interpreted in terms of formation of an additional μ -oxo bridge between Mn atoms.^{46,47} In another

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study EXAFS data were interpreted in terms of an increase in the PSII Mn₄ metal–metal distance, which was attributed to lengthening of the di μ -oxo bridges between Mn ions.⁴⁸ Among the proposed mechanisms for water oxidation, several account for S₂ to S₃ (or S₃ to S₀) advancement in terms of a significant core rearrangement, such as Mn–oxo rearrangement from a cubane to an adamantane core^{49,50} and rearrangement of a butterfly to a partial cubane core.^{35,51,52} Although EXAFS analysis of the active site of PSII excludes highly symmetric adamantane- or cubane-shaped Mn–oxo cores as accurate structural models of the S₀ to S₂ states, we conjecture that structural rearrangement of the Mn₄ OEC is an explanation for changes in the metal–metal distance proposed for advancement from S₂ to S₃ and S₃ to S₀. A core rearrangement demonstrated by us involves a shape shift from a dimer-of-dimers to an adamantane core.⁴³ Previously, we demonstrated that a dimer-of-dimers complex [Mn₄O₄(tphpn)₂](CF₃SO₃)₄ (**2**) (Htphpn = *N,N,N',N'*-tetra(2-pyridylmethyl)-2-hydroxypropane-1,3-diamine) is a good spectral model of the PSII S₁ state of the oxygen-evolving complex.^{41,42} Further investigation of the reactivity of **2** reveals that it undergoes dramatic structural changes concurrent with one-electron oxidation or reduction.^{43,53} In particular, oxidation of **2** from oxidation state (Mn^{III})₂(Mn^{IV})₂ to (Mn^{III})-(Mn^{IV})₃ results in a structural rearrangement to an adamantane-like core complex, [Mn₄O₄(tphpn)₂](CF₃SO₃)₂(ClO₄)₃ (**3**). We have also shown that **2** undergoes isomerization in solution without a redox change, as demonstrated by UV–vis and ¹H NMR spectroscopies.

The dimer-of-dimers and adamantane-shaped Mn–oxo cores exhibit additional reactivity relevant to water oxidation, such as protonation, reversible electron-transfer and proton-coupled electron transfer.^{21,25,41,53} Both electron- and proton-transfer chemistry are critical components of the Kok cycle⁵⁴ as well as various proposed mechanisms for water oxidation that emphasize the deprotonation of H₂O to form terminal or bridging OH[−] or O^{2−} ligands at the active site. Recent proposals suggest the participation of a Mn(IV)^{55,56} or Mn(V)^{57–61} terminal Mn=O group in the course of O–O bond formation.⁶² Furthermore, (Mn^{IV})₃Mn^V is one of the proposed oxidation state assignments for the OEC S₄

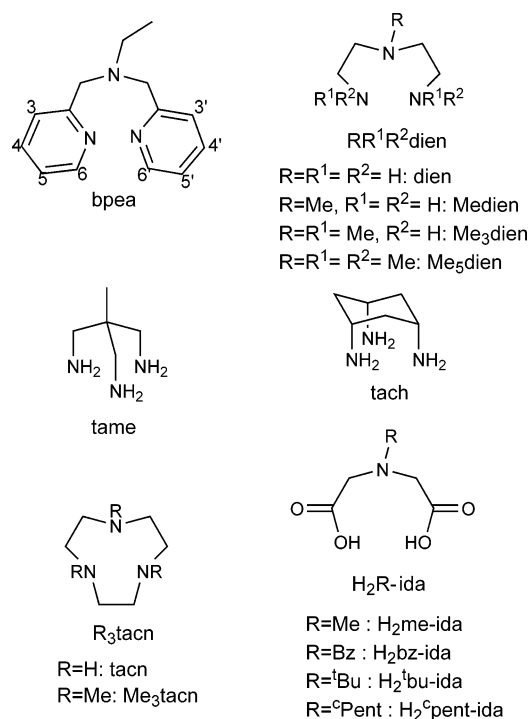


Figure 1. Ligands discussed in this paper.

state.^{57,63,64} For these reasons, an understanding of the factors that influence the protonation and redox behavior of tetranuclear manganese–oxo clusters is essential in order to activate a core toward substrate oxidation.

In an ongoing effort to understand the formation and physical properties of manganese–oxo clusters, we have extended our reactivity studies of Mn–oxo cores coordinated with *N,N*-bis(2-pyridylmethyl)ethylamine (bpea) (Figure 1).^{21,65–68} Previously, we showed that the adamantane-like complex [Mn₄O₆(bpea)₄](ClO₄)₄ (**1**) exhibits reversible protonation, electron-transfer, and proton-coupled electron transfer.²¹ Here we report the ligand substitution reactivity of **1**. Whereas self-assembly of aggregates frequently relies on assembling the thermodynamic product(s), the ligand-sub-

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Table 1. Designation of Compounds

[Mn ₄ O ₆ (bpea) ₄](ClO ₄) ₄	1
[Mn ₄ O ₆ (tacn) ₄](ClO ₄) ₄	4
[Mn ₄ O ₆ (bpea) ₂ (dien) ₂](ClO ₄) ₄	5
[Mn ₄ O ₆ (Medien) ₄](ClO ₄) ₄	6
[Mn ₄ O ₆ (tach) ₄](ClO ₄) ₄	7
[Mn ₄ O ₆ (bpea) ₂ (me-ida) ₂]	8
[Mn ₄ O ₆ (bpea) ₂ (bz-ida) ₂]	9
[Mn ₄ O ₆ (bpea) ₂ (bu-ida) ₂]	10
[Mn ₄ O ₆ (bpea) ₂ (pent-ida) ₂]	11

stituted product will be determined by kinetic as well as thermodynamic factors. Furthermore, we sought to use ligands such as iminodicarboxylates (Figure 1) that more closely approximate the coordination environment of PSII yet are too reactive under the highly oxidizing conditions typically utilized in self-assembly of high-valent manganese-oxo complexes. Also, we wished to explore the possibility of generating asymmetrically ligated clusters. Finally, it was hoped that substitution of the bpea ligand on the adamantane-shaped core with ligands possessing different characteristics would alter the reactivity of the [Mn₄O₆]⁴⁺ core, promote core rearrangement, and provide access to a Mn(V) species. Herein we report the synthesis and characterization of a series of adamantane-shaped [Mn₄O₆]⁴⁺ complexes, as designated in Table 1. In this paper, a comparison of spectroscopic and redox properties is presented as well as X-ray structure determinations for two members of the series. Furthermore, the pK_a value is established for two members of the series.

Experimental Section

Abbreviations. The following abbreviations are used throughout this paper: Fc/Fc⁺, ferrocene/ferricenium ion Fe^{II}(cp)₂/Fe^{III}(cp)₂⁺, where cp = cyclopentadienyl; TBAP, tetrabutylammonium perchlorate; bpea, *N,N*-bis(2-pyridylmethyl)ethylamine; bpta, *N,N*-bis(2-pyridylmethyl)-*tert*-butylamine; bispicen, *N,N'*-bis(2-methylpyridyl)-1,2-ethanediamine; tmpa, tris(2-methylpyridyl)amine; tren, 2,2',2''-triaminotriethylamine; tacn, 1,4,7-triazacyclononane; Me₃-tacn, 1,4,7-trimethyl-1,4,7-triazacyclononane; tame, 1,1,1-tris(aminomethyl)ethane; tach, *cis,cis*-1,3,5-triaminocyclohexane; dien, diethylenetriamine; Medien, *N'*-methyl-diethylenetriamine; Me₃dien, *N,N,N'*-trimethyl-diethylenetriamine; Me₅dien, *N,N,N',N'',N''*-pentamethyl-diethylenetriamine; me-ida, *N*-methyliminodiacetate; bz-ida, *N*-benzyliminodiacetate; bu-ida, *N-tert*-butyliminodiacetate; pent-ida, *N*-cyclopentyliminodiacetate

Materials. Acetonitrile used for synthesis was distilled from CaH₂. Acetonitrile used for electrochemical and UV-vis experiments was distilled from CaH₂ and then stored over 3 Å molecular sieves for at least 1 week prior to use. Propylene carbonate was dried over 4 Å molecular sieves for at least one week and vacuum distilled just prior to use. Deuterated acetonitrile (Cambridge Isotope Laboratories, Inc.) was dried in flame-dried glassware over activated 3 Å molecular sieves. Deuterated chloroform, methanol, and water (Cambridge Isotope Laboratories, Inc.) were used as received. Tacn, Me₃tacn, H₂me-ida, and H₂bz-ida were purchased from Aldrich and used as received. Dien, Medien, Me₃dien, and Me₅dien were purchased from Aldrich and distilled under vacuum prior to use. A mixture of *cis,cis*- and *cis,trans*-1,3,5-triaminocyclohexane was purchased from Ambinter. All other reagents were purchased and used as received. Electrochemical grade TBAP (Fluka) and AgClO₄ (Aldrich) were used as received. Paratone-N oil was obtained from Exxon. All chemicals used in this work were of reagent grade.

Physical Methods. Electronic spectra were collected at 298 K using a Cary 1E UV-vis spectrophotometer. ¹H NMR data were

collected at 298 K on a Varian Unity 300 MHz NMR spectrometer with a 100 kHz sweep width. All ¹H NMR spectra were background corrected using a first-order correction function. Peak widths at full-width half-maximum (fwhm) are in hertz. Values for chemical shifts (ppm) are the observed shifts referenced to the appropriate residual protic solvent peak (CHCl₃, 7.24 ppm; CHD₂CN, 1.94 ppm; CD₃OH, 4.78 ppm, CHD₂OD, 3.30 ppm; HOD, 4.68 ppm). IR spectra were recorded using a Nicolet 5DX FT-IR spectrometer using either a KBr disk or a solution cell containing an acetonitrile solution. Solid-state magnetic susceptibility measurements were performed on a Quantum Design SQUID magnetometer at either the Massachusetts Institute of Technology or Tufts University in the temperature range 2–300 K at a constant applied magnetic field of 0.5 T. Measurements at Tufts University were performed on powdered samples pressed into the small half of a gelatin capsule which was then sealed with the larger half of the capsule followed by Mylar tape. All data were corrected for the susceptibility of the empty sample container and Mylar tape, including its field dependence. Measurements at the Massachusetts Institute of Technology were performed on powdered samples pressed between cotton plugs inside a straw. All data were corrected for the susceptibility of the empty container, including its field dependence. Isothermal magnetization data were collected at 2, 5, and 10 K from 0.1 to 5.5 T. Solution magnetic susceptibility characteristics were determined by the NMR method^{69–71} at 298 K. Molar paramagnetic susceptibilities were obtained by using diamagnetic corrections ($\chi_d = -586 \times 10^{-6}$, -586×10^{-6} , -561×10^{-6} , and -648×10^{-6} cgs/mol for **4**, **7**, **8** and **9**, respectively) calculated from Pascal's constants.⁷² Elemental analyses were obtained from Desert Analytics, Tucson, AZ. Electrospray ionization mass spectrometry (ESI-MS) (typically 2×10^{-4} M in acetonitrile or methanol at a 3.5 kV nebulizer voltage) was performed on a Micromass Quattro mass spectrometer at the University of Illinois Mass Spectrometry Laboratory.

Electrochemistry. A BAS-100B Electrochemical Analyzer was used for electrochemical experiments. A platinum disk working electrode and a platinum wire auxiliary electrode were used to collect cyclic voltammograms in acetonitrile or propylene carbonate at a scan rate of 50 mV/s. An Ag/AgClO₄ electrode was used as the reference electrode. All electrochemical measurements employed 0.1 M TBAP as supporting electrolyte. Cyclic voltammetry of Fc in the appropriate solvent was determined during electrochemical analysis of compounds. The $E_{1/2}$ values of the Fc/Fc⁺ couple in acetonitrile and propylene carbonate were typically 106 and 72 mV, respectively. Potentials are reported versus the Fc/Fc⁺ couple.⁷³ All electrochemical measurements were performed under a dry and purified N₂ atmosphere. The potentials reported in this work are uncorrected for a junction contribution.

Ligand Synthesis. The ligand bpea was prepared as described elsewhere.^{66–68} Synthesis of *N*-cyclopentyliminodiacetic acid and *N-tert*-butyliminodiacetic acid, H₂pent-ida and H₂bu-ida, respectively, followed modifications⁷⁴ of the method of Berchet⁷⁵ and are given in detail in the Supporting Information. Synthesis of tame and tach was based on modifications⁷⁶ of the method of Fleischer

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et al.⁷⁷ Synthesis of tach is described in Supporting Information. **Caution!** Polyazides are potentially explosive.⁷⁸ Alternatively, tach was purified from a mixture of *cis,cis*- and *cis,trans*-1,3,5-triaminocyclohexane following the method of Wentworth⁷⁹ and is described in Supporting Information. The free base of tame and tach used for substitution chemistry were prepared under anhydrous conditions by dissolving the trihydrochloride salts in methanol and adding a stoichiometric amount of NaOMe and stirring briefly. The resulting solid was filtered off and the solvent removed by rotary evaporation to yield a white solid. This was dissolved in acetonitrile and filtered and the solvent removed to yield the free base as a fine white powder.

The *N*-alkyl quaternary ammonium salts (*n*-Bu₄N⁺ or Et₄N⁺) of H₂R-ida ligands were prepared by stoichiometric addition of an aqueous solution of either (*n*-Bu₄N)OH or (Et₄N)OH to an aqueous solution of H₂R-ida, where R denotes the substituent on the imine nitrogen atom. The majority of the solvent was removed by rotary evaporation to obtain a viscous oil and the final drying was done on a vacuum line. The dried *N*-alkyl quaternary ammonium salts of H₂R-ida are hygroscopic and were recrystallized under anhydrous conditions. See Table S1 for yields, elemental analyses, and ¹H NMR data for these ligands.

Complex Synthesis. [Mn₄O₆(bpea)₄](ClO₄)₄ (**1**), [Mn₄O₆(bpea)₄](CF₃SO₃)₄, and [Mn₄O₆(bpea)₄]Br₄ were prepared as described previously.²¹

[Mn₄O₆(tacen)₄](ClO₄)₄ (**4**). An acetonitrile solution (1.0 mL) of tacn (0.080 g, 0.616 mmol) was added to an acetonitrile solution (25 mL) of **1** (0.222 g, 0.137 mmol) over 10 min. The reaction mixture was allowed to stir for 1 h and then the solution was concentrated to about 1 mL by rotary evaporation. The product was precipitated by dropwise addition of the acetonitrile solution to 3 mL of vigorously stirred diethyl ether. The dark purple precipitate was collected by filtration and washed with diethyl ether and dried in vacuo to give 0.156 g (0.127 mmol, 93%) of **4** as a dark purple powder. Diffusion of chloroform into an acetonitrile solution (3 mL) of **4** (0.156 g, 0.127 mmol) at room temperature gave purple hexagonal plates of **4** (0.148 g, 0.121 mmol, 88%). See Table S2 for yields, elemental analyses and ESI-MS data, Table S3 for UV–vis, E_{1/2}, and IR data, and Table S4 for ¹H NMR data for this and other compounds in this section.

Preparation of [Mn₄O₆(tacen)₄](CF₃SO₃)₄ was done in an entirely analogous manner using [Mn₄O₆(bpea)₄](CF₃SO₃)₄. Complex [Mn₄O₆(tacen)₄](CF₃SO₃)₄ was crystallized from vapor diffusion of chloroform into an acetonitrile solution of it at room temperature.

[Mn₄O₆(dien)₂(bpea)₂](ClO₄)₄ (**5**). An acetonitrile solution (2.5 mL) of dien (0.040 g, 0.385 mmol) was added to an acetonitrile solution (20 mL) of **1** (0.250 g, 0.154 mmol) over 30 min with an addition funnel. The solution was allowed to stir for an additional 3 h and then the solution was concentrated to 2 mL by rotary evaporation. The product was precipitated by dropwise addition of the acetonitrile solution to 5 mL of vigorously stirred diethyl ether. The dark brown precipitate was collected by filtration and washed with diethyl ether and dried in vacuo to give 0.171 g (0.125 mmol, 81%) of **5** as a dark brown powder. Diffusion of CHCl₃ into an acetonitrile solution (4 mL) of **5** (0.171 g, 0.125 mmol) at room temperature gave thin dendritic black plates of **5** (0.166 g, 0.121 mmol, 79%).

[Mn₄O₆(Medien)₄](ClO₄)₄ (**6**). An acetonitrile solution (2 mL) of Medien (0.084 g, 0.704 mmol) was added to an acetonitrile solution (20 mL) of **1** (0.254 g, 0.156 mmol) over 10 min. The reaction was allowed to stir for an additional 30 min and then the solution was concentrated to 1 mL by rotary evaporation. The product was precipitated by dropwise addition of the acetonitrile solution to 3 mL of vigorously stirred diethyl ether. The dark brown precipitate was collected by filtration and washed with diethyl ether and dried in vacuo to give 0.130 g (0.110 mmol, 70%) of **6** as a dark brown powder. Diffusion of CHCl₃ into an acetonitrile solution (4 mL) of **6** (0.130 g, 0.110 mmol) at room temperature gave microcrystalline **6** (0.116 g, 0.098 mmol, 62%).

[Mn₄O₆(tach)₄](ClO₄)₄ (**7**). A methanol solution (0.5 mL) of tach (0.100 g, 0.773 mmol) was added to an acetonitrile solution (20 mL) of **1** (0.167 g, 0.103 mmol) over 10 min. The reaction was allowed to stir for 6 h and then the solution was concentrated to dryness using rotary evaporation. The dark purple precipitate was triturated with EtOH to remove excess tach and dried in vacuo to give 0.126 g (0.102 mmol, 99%) of **7** as a dark purple powder. Diffusion of diethyl ether into an acetonitrile solution (3 mL) of **7** (0.126 g, 0.102 mmol) at –20 °C gave purple hexagonal plates of **7** (0.108 g, 0.088 mmol, 85%).

Ligand substitution reactions with hygroscopic [Et₄N]₂[R-ida] and [*n*-Bu₄N]₂[R-ida] ligands were performed under prepurified argon with standard glovebox techniques.

[Mn₄O₆(bpea)₂(me-ida)₂] (**8**). An acetonitrile solution (5 mL) of [*n*-Bu₄N]₂[me-ida] (0.214 g, 0.340 mmol) was added dropwise to a stirred acetonitrile solution (20 mL) of **1** (0.250 g, 0.154 mmol) over 15 min. The reaction was allowed to stir for an additional 15 min, after which time a light green precipitate was allowed to settle, leaving a faint red solution. The crude product was filtered under ambient conditions, washed with acetonitrile, and dried under vacuum to give 0.114 g (70%) of **8**. Vapor diffusion of acetone into an aqueous solution (3 mL) of **8** (0.114 g, 0.107 mmol) yielded fine green needles of **8** (0.0627 g, 0.059 mmol, 55%) after 3 days at room temperature.

[Mn₄O₆(bpea)₂(^cpent-ida)₂] (**11**). An acetonitrile solution (5 mL) of [Et₄N]₂[^cpent-ida] (0.225 g, 0.489 mmol) was added dropwise to a stirred acetonitrile solution (15 mL) of **1** (0.318 g, 0.196 mmol) over 15 min. The reaction was allowed to stir for an additional 15 min, after which time a light green precipitate was allowed to settle, leaving a red-brown solution. The crude product was filtered under ambient conditions, washed with acetonitrile, and dried under vacuum to give 0.135 g (0.116 mmol, 59%) of **11**. The crude product was dissolved in 3 mL of MeOH and filtered. Diffusion of Et₂O into a MeOH solution (3 mL) of **11** (0.135 g, 0.116 mmol) at –20 °C gave thin rectangular plates (0.123 g, 0.106 mmol, 54%).

Complexes **9** and **10** were synthesized and crystallized according to the procedure for **11** and are described in the Supporting Information.

¹H NMR Titration. Protonation of **8 and **11**.** In a typical titration, a solution of **8** in D₂O (0.4 mL, 9.0 mM) was prepared and transferred to an NMR tube. Protonation of **8** was accomplished by addition of aliquots of HClO₄ (1.0 μL, 1.0 M in CD₃CN) with a gastight syringe through the septum seal of the NMR tube. Generation of 8H(ClO₄) was considered complete when additional aliquots of HClO₄ gave no further change in the ¹H NMR spectrum. A ¹H-NMR-monitored titration of **11** was carried out in an entirely analogous fashion in MeOD or D₂O.

Spectrophotometric Titration. Protonation of **8 and **11**.** Titration of aqueous solutions of **8** and **11** was monitored spectrophotometrically and with a pH electrode. In a typical titration, the pH and absorbance spectrum of **8** (2 mL of a 4.31 × 10^{–4} M

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Table 2. Crystallographic Data for $[\text{Mn}_4\text{O}_6(\text{tach})_4](\text{ClO}_4)_4 \cdot 3\text{CH}_3\text{CN} \cdot 4.5\text{H}_2\text{O}$ and $[\text{Mn}_4\text{O}_6(\text{bpea})_2(\text{pent-ida})_2] \cdot 7\text{MeOH}$

	$7 \cdot 3\text{CH}_3\text{CN} \cdot 4.5\text{H}_2\text{O}$	$11 \cdot 7\text{MeOH}$
empirical formula	$\text{C}_{30}\text{H}_{78}\text{Cl}_4\text{Mn}_4\text{N}_{15}\text{O}_{26.5}$	$\text{C}_{53}\text{H}_{88}\text{Mn}_4\text{N}_8\text{O}_{21}$
formula weight, g/mol	1434.49	1393.05
crystal system	cubic	monoclinic
space group	$Fm\bar{3}m$	$C2/c$
a , Å	23.934(6)	10.543(2)
b , Å	23.934(6)	25.198(4)
c , Å	23.934(6)	24.295(4)
α , deg	90	90.
β , deg	90	90.28(2)
γ , deg	90	90.
volume, Å ³	13711(6)	6454.1(2)
Z	8	4
$\rho(\text{calc})$, g/cm ³	1.390	1.434
θ range, deg	1.47–26.39	1.82–28.19
reflections collected	22104	8775
independent reflections	765 [$R(\text{int}) = 0.1499$]	6424 [$R(\text{int}) = 0.0303$]
data/restraints/parameters	765/1/51	6264/1/368
goodness-of-fit of F^2	1.053	1.088
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0691$, $wR2 = 0.2116$	$R1 = 0.0634$, $wR2 = 0.1216$

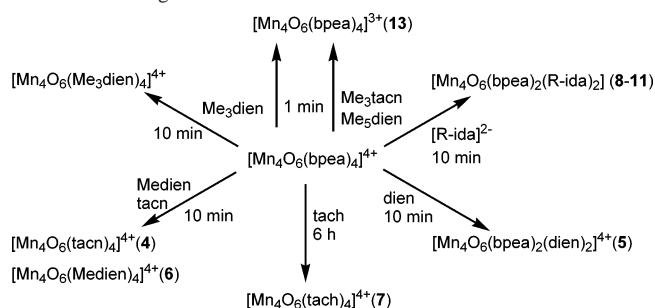
aqueous stock solution) was measured following addition of an acid such as perchloric acid ($\text{p}K_a = -1.7$, the $\text{p}K_a$ of H_3O^+), triflic acid ($\text{CF}_3\text{SO}_3\text{H}$, $\text{p}K_a = -1.7$), or trifluoroacetic acid ($\text{p}K_a = 0.5$).⁸⁰ Acid was added until there was no further change in the absorbance spectrum. The data were fit to the following expression, derived for the reaction $\text{B} + \text{H}^+ \rightleftharpoons \text{HB}^+$

$$A_\lambda = C_0 \left(\frac{(\epsilon_{\text{HB}}^\lambda) 10^{-\text{pH}} + (\epsilon_{\text{B}}^\lambda) 10^{-\text{p}K_a}}{10^{-\text{pH}} + 10^{-\text{p}K_a}} \right) \quad (1)$$

where A_λ is the absorbance at a selected wavelength, C_0 is the initial concentration of the complex, and $\epsilon_{\text{B}}^\lambda$ and $\epsilon_{\text{HB}}^\lambda$ are the extinction coefficients of the complex and its protonated form, respectively, at the selected wavelength. Spectrophotometric titrations of **8** and **11** were monitored at 515 nm and nonlinear least-squares fitting of eq 1 to the experimental data used 1795 and 2422 for $\epsilon_{\text{B}}^\lambda$ and $\epsilon_{\text{HB}}^\lambda$, respectively, for **8** and 1798 and 2361 for $\epsilon_{\text{B}}^\lambda$ and $\epsilon_{\text{HB}}^\lambda$, respectively, for **11**.

X-ray Crystallography. Compound **7** crystallizes as $[\text{Mn}_4\text{O}_6(\text{tach})_4](\text{ClO}_4)_4 \cdot 3\text{CH}_3\text{CN} \cdot 4.5\text{H}_2\text{O}$ in the cubic space group $Fm\bar{3}m$ with eight molecules in the unit cell and compound **11** crystallizes as $[\text{Mn}_4\text{O}_6(\text{bpea})_2(\text{pent-ida})_2] \cdot 7\text{MeOH}$ in the monoclinic space group $C2/c$ with four molecules in the unit cell. Relevant crystal data are summarized in Table 2.

Single crystals of **7** suitable for structure determination were obtained by diffusion of diethyl ether into an acetonitrile solution of **7** at -20°C . Single crystals of **11** suitable for structure determination were obtained by diffusion of diethyl ether into a methanol solution of **11** at -20°C . Crystals of each were taken from the mother liquor, coated with Paratone-N oil, mounted on a glass fiber with Apiezon-T grease, and immediately transferred to the dinitrogen cold stream. Data for **7** were collected using a Bruker diffractometer equipped with a SMART-APEX CCD (charge-coupled device) detector and data for **11** were collected using a Bruker diffractometer equipped with a SMART CCD detector. The instruments used Mo K α radiation ($\lambda = 0.71073$ Å) and included a LT-3 low-temperature apparatus operating at 193 K. Data were measured using omega scans of 0.3° per frame for 30 s, such that a hemisphere was collected. A total of 1271 frames were collected with a maximum resolution of 0.75 Å. The first 50 frames were

Scheme 1. Ligand Substitution Reactions of **1** in Acetonitrile

recollected at the end of data collection to monitor for crystal decay. Crystals used for the diffraction studies showed no decomposition during data collection.

Cell parameters were retrieved using SMART⁸¹ software and refined using SAINT⁸² on all observed reflections. Data reduction was performed using the SAINT software, which corrects for L_p and decay. Absorption corrections were performed with the SADABS Program,⁸³ supplied by George Sheldrick. The structures were solved by direct methods using SHELXS-97⁸⁴ and refined by least-squares methods on F^2 in SHELXL-97,⁸⁵ incorporated in SHELXTL-PC V 5.10.⁸⁶ All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated by geometrical methods and refined using a riding model. All drawings presented here are made using 30% probability thermal ellipsoids.

Results and Discussion

Synthesis. Ligand substitution reactions of **1** are outlined in Scheme 1. Complex **1** was synthesized by comproportionation of Mn(II) and Mn(VII) starting materials in the presence of the bpea ligand.²¹ We speculate that a similar synthetic approach with the primary amine and iminodicarboxylate ligands used here would have resulted in ligand oxidation in the course of self-assembly. While ligand oxidation during self-assembly can be a useful synthetic tool in the formation of new complexes, we pursued ligand substitution reactions of **1** as an initial approach.

It was anticipated that ligand substitution reactions of this core would be slow. This is because the $\text{Mn}^{\text{IV}} d^3$ ions, like the substitutionally inert Cr^{III} ,^{87–89} enjoy a considerable ligand field stabilization energy (LFSE) and that ligand substitution by a dissociative (D) or interchange dissociative (I_d) mech-

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- (88) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217–268.
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anism through a trigonal bipyramidal transition state would involve a significant loss of LFSE.⁹⁰ It is unlikely that ligand substitution would proceed by an associative (A) or interchange associative (I_a) mechanism, through a 7-coordinate transition state, due to the bulky nature of the tridentate ligands. In addition, the tridentate ligands of **1** impart additional stability against ligand substitution due to the chelate effect. Also, it was unclear whether ligand substitution reactions with **1** would proceed with retention of the [Mn₄O₆]⁴⁺ core structure or whether substitution would promote core rearrangement, aggregation, or fragmentation. Our investigations have shown that reaction of **1** with a variety of tridentate amine and iminodicarboxylate ligands in acetonitrile at room temperature produces derivative clusters **4**–**11** generally on the order of 10 min with retention of core nuclearity and oxidation state, as monitored by UV–vis and ¹H NMR spectroscopy. Of these complexes, only **4** had been synthesized previously.^{18,20,91} Although it was not attempted, it is possible that self-assembly of several of the amine complexes, such as **6** and **7**, would have been achieved by air oxidation of a basic solution of Mn(II) and the respective ligands, analogous to the synthesis of **4**,^{18,20} [Mn₄O₅(OH)(tame)₄](CF₃SO₃)₅,²⁰ [Mn₂O₂(cyclam)₂](ClO₄)₃,⁹² and [Mn₂O₂(tren)₂](CF₃SO₃)₃.⁹³

Reaction of **1** with the amine ligands in acetonitrile resulted in either ligand substitution, one-electron reduction of **1** to form [Mn₄O₆(bpea)₄](ClO₄)₃ (**13**),^{21,23,24} or both. For example, reaction of **1** in acetonitrile (5 × 10^{−4} M) with 4.2 equiv of tacn typically produced the ligand substitution product **4** in about 10 min. On occasion, however, nonstoichiometric one-electron reduction of **1** occurred during ligand substitution reactions, requiring considerably longer times (about 2.5 h for completion, at about 86% yield) to form **4**. ¹H NMR confirmed the observation of rapid, yet partial, initial core reduction to **13** and the formation of tacnH⁺, followed by slower ligand substitution over a few hours. On the other hand, reaction of **1** with the tertiary amine Me₃tacn produced only **13** and Me₃tacnH⁺ in quantitative yield, as noted previously.²¹ Reactions of **1** with the primary amines tame and tach exhibited much slower substitution kinetics. ¹H NMR spectra of the reaction of **1** (1.2 × 10^{−2} M) with the primary amine tame (up to 15 equiv) over times on the order of 24 h suggest partial substitution; thus, this reaction was not pursued further. On the other hand, reaction of **1** (5.15 × 10^{−3} M) with 8 equiv of the more rigid amine tach, which is conformationally predisposed for facial coordination, proceeds cleanly to the tach analogue **7** for times on the order of 6 h. Reaction of **1** with 3–8 equiv of dien resulted in isolation of the mixed ligand product [Mn₄O₆(bpea)₂(dien)₂](ClO₄)₄ (**5**), the structure of which has been crystallographically established and confirmed by mass

spectrometry. Reaction of **1** with Medien resulted in isolation of the fully substituted product [Mn₄O₆(Medien)₄](ClO₄)₄ (**6**) in about 10 min, which was also confirmed by mass spectrometry. Reaction of **1** with Me₃dien gave a mixture of [Mn₄O₆(Me₃dien)₄](ClO₄)₄ (observed by electrospray MS [M – ClO₄]⁺ = 1195.5; expected 1195.1) and **13** (observed by ¹H NMR), while reaction of **1** with Me₃dien gave only **13**.

The oxidation of tertiary amines by inorganic complexes has been explored both as a preparative tool^{73,94,95} and for its enzymatic relevance.^{95,96} Although often mechanistic details remain unclear, it is generally accepted that the reducing power of an amine is determined by its pK_a and not by its oxidation potential and that coordination of the amine nitrogen to the metal complex is a critical step in the electron transfer.^{94,95} Most recently, oxidative transformations of amines employing transition metal catalysts, such as Ru or Co, and molecular oxygen are receiving increasing attention.^{97,98} In these reports the proposed transformations involve coordination of the tertiary amine and molecular oxygen to the metal center in the initial activation steps. A recent report of the noncatalytic oxidation of tertiary amines using a Mn^{III}Mn^{IV} complex proposes coordination of the amine to a metal center, although dioxygen activation is thought to occur via an amine α-radical to form an α-amino peroxide.⁹⁹

Substitution chemistry of **1** with *N*-alkyl quaternary ammonium salts of *N*-substituted iminodicarboxylate ligands resulted in the neutral mixed-ligand complexes [Mn₄O₆(bpea)₂(R-ida)₂]. There was no apparent reaction between H₂R-ida and **1** in acetonitrile for periods up to 13 h according to UV–vis and ¹H NMR data. *N*-Alkyl quaternary ammonium salts, rather than Na⁺ or K⁺ salts, were chosen for their greater solubility. Attempts to prepare a [Mn₄O₆(R-ida)₄]^{4−} complex were unsuccessful. The mixed ligand complexes precipitated on the order of minutes from an acetonitrile solution of **1** containing greater than 4 equiv of the R-ida ligand. Ligand substitution in methanol, in which the starting material [Mn₄O₆(bpea)₄]Br₄ or **1** (the latter at much lower solubility) and complexes **8**–**11** are soluble gave a reddish solution upon addition of excess R-ida ligand within minutes, followed by gradual bleaching to a colorless solution and precipitation of flocculant material after about 10 h. It may be that the fully substituted product [Mn₄O₆(R-ida)₄]^{4−} is formed in methanol and that it is unstable.

Structures. The crystal structures of the full cation of **7** and the neutral complex **11** are shown in Figure 2, parts a and b, respectively. Figure 3 shows the [Mn₄O₆]⁴⁺ cores only. The Mn and oxide O atoms in the crystal structures of **7** and **11** define the adamantane skeleton. The Mn atoms occupy the apexes of a tetrahedron and the O atoms occupy

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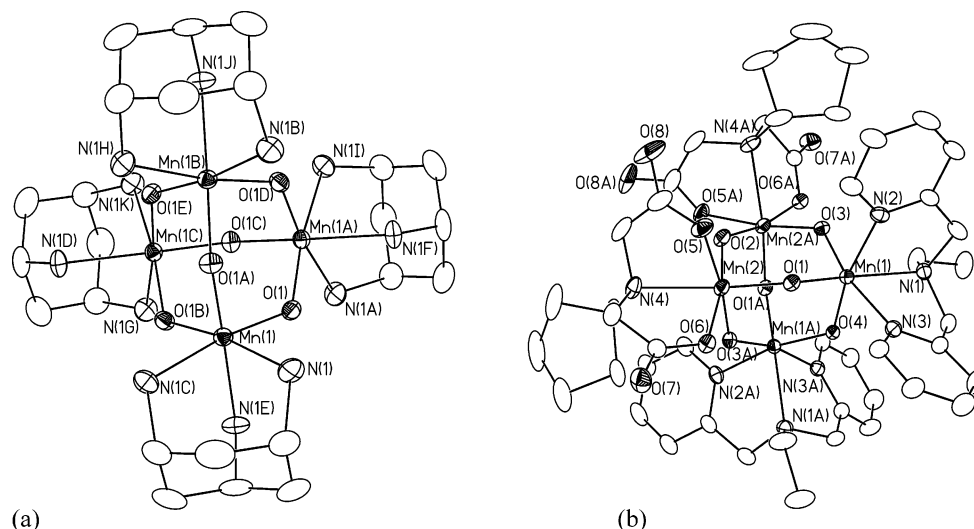


Figure 2. ORTEP plots of the structures and atom labeling schemes of (a) **7**(ClO₄)₄ and (b) **11** showing 30% probability thermal ellipsoids. Hydrogen atoms (and perchlorate counterions for **7**) are omitted for clarity.

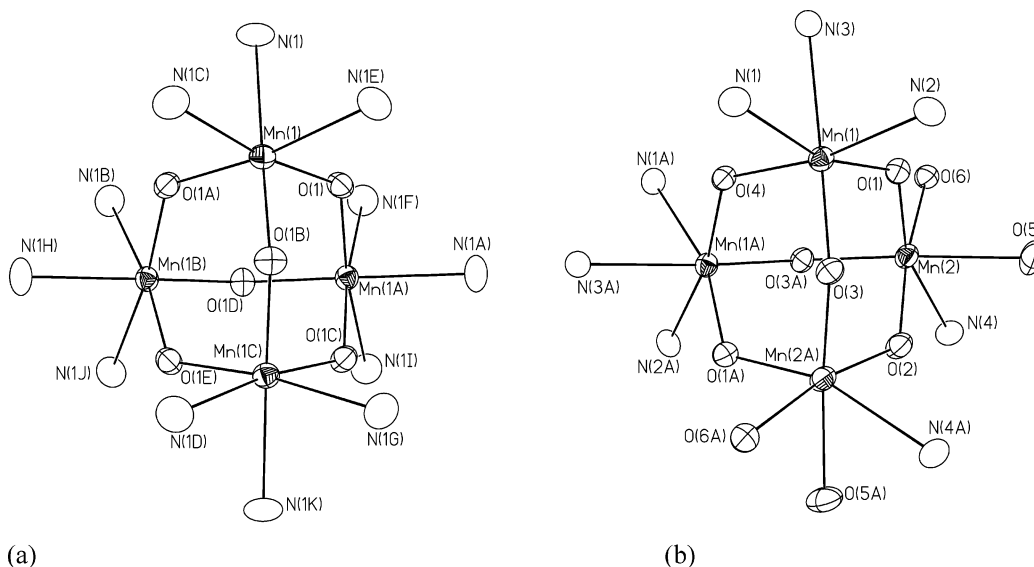


Figure 3. ORTEP plots of the {Mn₄O₆} cores of (a) **7** and (b) **11** showing 30% probability thermal ellipsoids. Carbon and hydrogen atoms (and perchlorate counterions for **7**) are omitted for clarity.

Table 3. Selected Bonds Distances (Å) and Angles (deg) for [Mn₄O₆(tach)₄](ClO₄)₄·3CH₃CN·4.5H₂O

bond distances		bond angles	
Mn(1)—O(1)	1.808(3)	O(1A)—Mn(1)—O(1)	98.0(2)
Mn(1)—N(1)	2.096(7)	Mn(1)—O(1)—Mn(1A)	129.3(4)
N(1)—C(1)	1.486(11)		
C(2)—C(1)	1.493(8)		

the apexes of an octahedron. Each Mn atom is coordinated to three bridging oxide O atoms and three atoms from the terminal ligands in pseudo-octahedral geometry. Complex **7** exhibits crystallographically imposed *T_d* point symmetry, rendering all the Mn atoms, bond lengths, and bond angles equivalent. The Mn—O_{oxo} bond length of 1.808(3) Å and the Mn—O—Mn angle of 129.3(4)° for **7** (Table 3) are similar to those of **4** [1.796(1) Å and 128.0(1)°, respectively]²⁰ and are generally consistent with metric data for other Mn^{IV}—O_{oxo} complexes. The tach ligand displays local 3-fold symmetric coordination to the manganese ions in **7**, with a Mn—N distance of 2.101(6) Å, very similar to the average

tach Mn—N distance of 2.092(1) Å for **4** and significantly shorter than the Mn—N_{alkyl} bond length of 2.196(2) Å for the bpea ligand of **1**.

In contrast to the high point symmetry of **7**, **11** exhibits only *C₂* point symmetry. This symmetry results in four types of bridging oxo ligands, two of which lie along the crystallographic *C₂* axis [O(2) and O(4) in Figure 3b]. Oxo bridge O(2) is trans to the carboxylate oxygen atoms of the ‘pent-ida ligands and has a Mn—O bond length of 1.7986(17) Å. Its Mn—O—Mn angle of 133.5(2)° (Table 4) is the largest angle measured thus far for a Mn—oxo adamantane shaped core. Oxo bridge O(4) is trans to two pyridyl nitrogen atoms of the bpea ligands and has a Mn—O bond length of 1.798(2) Å and a Mn—O—Mn angle of 127.2(2)°.

Of the four oxo bridges lying in the plane perpendicular to the *C₂* axis, two [O(1) and O(1A)] are trans to a bpea tertiary amine nitrogen atom and a ‘pent-ida tertiary amine nitrogen atom, with a Mn—O—Mn angle of 127.95(16)° and

Table 4. Selected Bonds Distances (Å) and Angles (deg) for $[\text{Mn}_4\text{O}_6(\text{bpea})_2(\text{'pent-ida'})_2]\cdot 7\text{MeOH}$

bond distances		bond angles	
Mn(1)–O(1)	1.780(3)	O(1)–Mn(1)–O(3)	100.30(13)
Mn(1)–O(3)	1.792(3)	O(1)–Mn(1)–O(4)	98.51(12)
Mn(1)–O(4)	1.7980(18)	O(3)–Mn(1)–O(4)	98.14(11)
Mn(1)–Mn(2)	3.2114(10)	O(1)–Mn(2)–O(3A)	97.19(13)
Mn(1)–Mn(1A)	3.2207(13)	O(1)–Mn(2)–O(2)	98.47(12)
Mn(2)–O(1)	1.794(3)	O(3A)–Mn(2)–O(2)	94.08(12)
Mn(2)–O(3A)	1.798(3)	O(1)–Mn(2)–O(5)	89.43(14)
Mn(2)–O(2)	1.7986(17)	O(3A)–Mn(2)–O(5)	172.69(14)
O(2)–Mn(2A)	1.7986(17)	O(2)–Mn(2)–O(5)	87.98(13)
O(3)–Mn(2A)	1.798(3)	O(1)–Mn(2)–O(6)	90.33(12)
O(4)–Mn(1A)	1.7980(18)	O(3A)–Mn(2)–O(6)	90.01(12)
		O(2)–Mn(2)–O(6)	169.75(14)
		O(5)–Mn(2)–O(6)	86.84(13)
		Mn(2A)–O(2)–Mn(2)	133.5(2)
		Mn(1)–O(3)–Mn(2A)	130.36(17)
		Mn(1)–O(4)–Mn(1A)	127.2(2)
		Mn(1)–O(1)–Mn(2)	127.95(16)

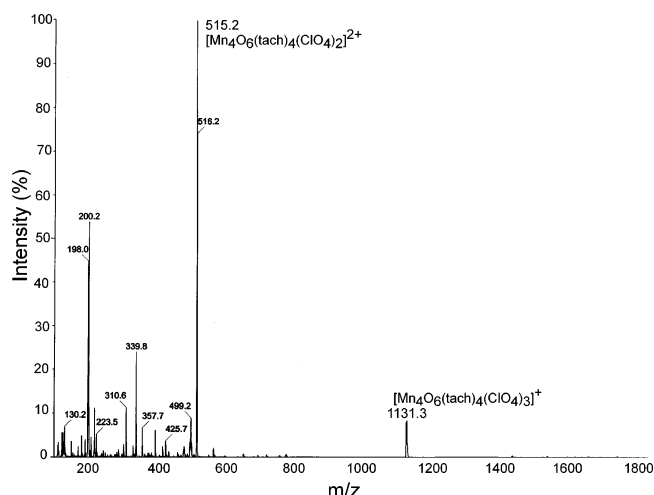
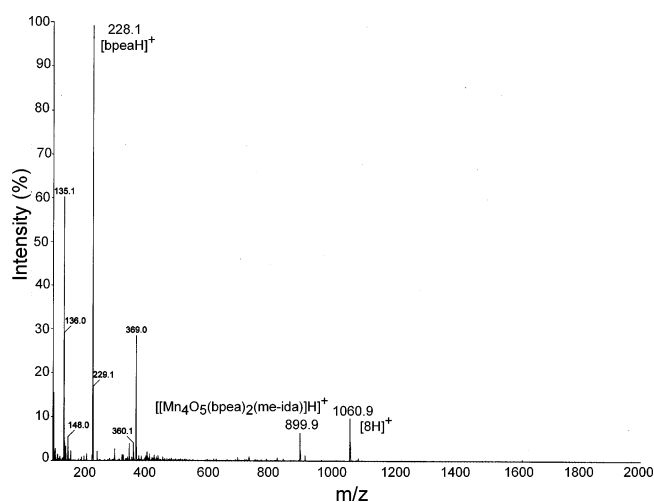
a Mn–O bond length of 1.780(2) Å. The remaining two bridges [O(3) and O(3A)] are trans to a pyridyl nitrogen atom and a carboxylate oxygen atom of bpea and 'pent-ida ligands, respectively, with a Mn–O–Mn angle of 130.36(17)° and an average Mn–O bond length of 1.792(2) Å. All of these bond lengths are comparable to those of **1**, which is characterized by four Mn–O bonds 1.806(1) Å long and two Mn–O bonds 1.786(2) Å long.

The Mn–N bond lengths of the bpea ligands of **11** are similar to those of **1**: an average Mn–N_{alkyl} bond length of 2.173(4) Å and two kinds of Mn–N_{py} bonds, a "short" Mn–N_{py} bond with an average length of 2.080(4) Å and a slightly longer Mn–N_{py} bond with an average length of 2.094(3) Å. Longer Mn–N_{alkyl} bonds¹⁰⁰ are observed for other structurally characterized compounds whose multidentate ligands are comprised of both alkyl and pyridyl nitrogen atoms, including bpea,^{65,66,68} bpta,⁶⁸ bispicen,^{101,102} and tmpa.¹⁰³ The four carboxylate Mn–O bonds of the 'pent-ida ligand of **11** [average length of 2.024(3) Å] are somewhat longer than similar Mn^{IV}–O bonds for other terminal carboxylate ligand Mn complexes (1.980–1.999 Å).^{104–106}

The average Mn···Mn distance of **11** [3.2161(11) Å] is somewhat shorter than the corresponding distance in **4** [3.227(2) Å], **7** (3.269 Å), and **1** [3.248(1) Å].

Physical Properties. Mass Spectrometry. Electrospray ionization mass spectrometry data are summarized in Table S2 and all spectra can be found in the Supporting Information. The ESI mass spectra of **7** and **8** are shown in Figures 4 and 5, respectively.

The substitution products can be divided into two groups: the cations and the neutral species. The $[\text{Mn}_4\text{O}_6]^{4+}$ cations readily lose an anion to form $[\text{M} - \text{ClO}_4]^+$ species. The tach

**Figure 4.** Positive ion electrospray ionization mass spectrum of **7** in acetonitrile at unit resolution.**Figure 5.** Positive ion electrospray ionization mass spectrum of **8** in water/methanol (10%) at unit resolution.

(**7**) and tachn (**4**) complexes behave similarly, with $[\text{M} - \text{ClO}_4]^+$ and $[\text{M} - 2\text{ClO}_4]^{2+}$ being the predominant species, but otherwise exhibiting very little fragmentation. The mass spectrum of complex **6** shows striking similarity to those of the strong amine donor ligand complexes **4** and **7**, with major peaks at $[\text{M} - \text{ClO}_4]^+$ (1082.9), $[\text{M} - 2\text{ClO}_4]^{2+}$ (491.7), $[\text{M} - 3\text{ClO}_4]^{3+}$ (294.6), and $[\text{M} - 4\text{ClO}_4]^{4+}$ (196.1). The mass spectrum for the mixed dien/bpea complex (**5**), with a major peak at $[\text{M} - \text{ClO}_4]^+$ (1275.2), showed similar behavior to that of **1**, which exhibited a much greater tendency toward core fragmentation in the gas phase.²¹

The mass spectra of the $[\text{Mn}_4\text{O}_6(\text{bpea})_2(\text{R-ida})_2]$ complexes are similar to each other, exhibiting prominent species at $[\text{M} + \text{H}]^+$ (1060.9, 1213.4, 1145.4, and 1169.5 for **8**, **9**, **10**, and **11**, respectively) and $[\text{M} + \text{Na}]^+$ (1235.4, 1167.3, and 1191.4 for **9**, **10**, and **11**, respectively), as well as prominent peaks that correspond to addition of R-ida²⁻ ligands and peaks corresponding to loss of CO₂.

Electronic and Vibrational Spectroscopy. The IR spectra of the $[\text{Mn}_4\text{O}_6]^{4+}$ cores show a number of bands attributable to the different ligands and the ClO₄⁻ anion (~1119 and

- (100) The comparison is among Mn^{IV}–N_{alkyl} and Mn^{IV}–N_{py}, which are trans to μ-O ligands.
- (101) Collins, M. A.; Hodgson, D. J.; Michelson, K.; Towle, D. K. *J. Chem. Soc., Chem. Commun.* **1987**, 1659–1660.
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625 cm^{-1}),¹⁰⁷ and each compound also exhibits intense bands attributed to the Mn–O–Mn stretch in the region between about 695 and 732 cm^{-1} (Table S3).^{21,22} An intense band for **1** at 708 cm^{-1} is near the middle of this range, while the corresponding bands for the substitution products **4** (732 cm^{-1}) and **10** (695 cm^{-1}) delineate the extremes.

The mixed ligand R-ida series also display two intense bands around 1620 and 1380 cm^{-1} attributed to the coordinated carboxylate ligand.¹⁰⁷ The mode of coordination of R-ida is readily determined from the values of $\nu_a(\text{COO})$ and $\nu_s(\text{COO})$ and the value of $\Delta = [\nu_a(\text{COO}) - \nu_s(\text{COO})]$.^{107,108} The infrared spectra of the $[\text{Mn}_4\text{O}_6(\text{bpea})_2(\text{R-ida})_2]$ series all have a value of Δ between 240 and 244 cm^{-1} , which is characteristic of unidentate coordination of the carboxylate ion. As anticipated, unidentate coordination of the carboxylate moieties of the ‘pent-ida ligand to the Mn ions has been verified for **11** by X-ray structural analysis, substantiating the structurally characterized sample as representative of the bulk material. A survey of representative metalloprotein crystal structure determinations¹⁰⁹ reveals that unidentate carboxylate can bind either syn or anti with respect to the lone pairs of electrons. As expected, ‘pent-ida ligation to the Mn ion is anti unidentate.

The electronic spectra of all the complexes are similar to each other, with the most notable feature in the absorption spectrum being the putative $\text{O} \rightarrow \text{Mn}^{\text{IV}}\text{d}\pi^*$ charge-transfer band in the range 546 to 591 nm, as well as a number of less intense bands at 990–1000 nm for all of the complexes, most likely d–d transitions (Table S3). The fully substituted strong N-donor ligand complexes (**4**, **6**, and **7**) also exhibit a very weak shoulder at about 750 nm.

Electrochemistry. The ligands described here stabilize the adamantane-shaped $[\text{Mn}_4\text{O}_6]$ core in the $\text{Mn}^{\text{III}}(\text{Mn}^{\text{IV}})_3$, $(\text{Mn}^{\text{IV}})_4$, and $\text{Mn}^{\text{V}}(\text{Mn}^{\text{IV}})_3$ oxidation states. Ligand substitution on **1** greatly decreased the reduction potential of the (IV, IV, IV, IV)/(III, IV, IV, IV) redox couple from $E_{1/2} = -0.28$ to -1.03 V for **9**, a shift of 750 mV. Cyclic voltammograms of **7** and **9** are shown in Figures 6 and 7, respectively, and all electrochemical data are summarized in Table S3.

Particularly noteworthy is the substantial inductive effect of the substituted iminodicarboxylates, as shown in the plot of $\text{O} \rightarrow \text{Mn}^{\text{IV}}\text{d}\pi^*$ LMCT energy versus $E_{1/2}$ (Figure 8). Figure 8 also illustrates the differentiation of the strong σ -donor amines and the strong π -donor carboxylates with respect to LMCT. Tuning of the redox potentials of the $[\text{Mn}_4\text{O}_6]^{4+}$ complexes follows a ranking of the ancillary ligands, as determined for a number of mononuclear ruthenium and dinuclear manganese complexes, based on their redox potentials: $\text{RO}^- > \text{RCO}_2^- > \text{R}_3\text{N} > \text{R}_2\text{NH} > \text{pyridine}$.^{110–113}

(107) Nakamoto, K., *Infrared and Raman Data of Inorganic and Coordination Compounds*, 5 ed.; John Wiley: New York, 1997; Vols. A & B.

(108) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227–250.

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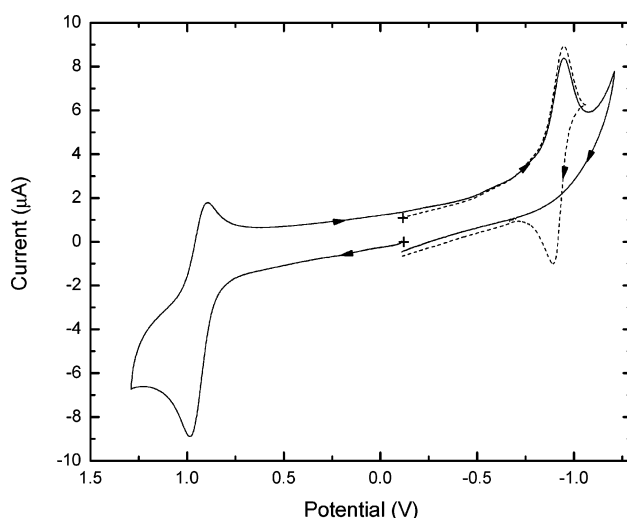


Figure 6. Cyclic voltammograms of an acetonitrile solution 1.20 mM in **7**(ClO₄)₄ and 0.2 M in TBAP illustrating quasireversible oxidation and reduction. The two scans have the same starting potential (denoted with +) but differ by scan direction and scan window. Potentials are versus Fc/Fc⁺.

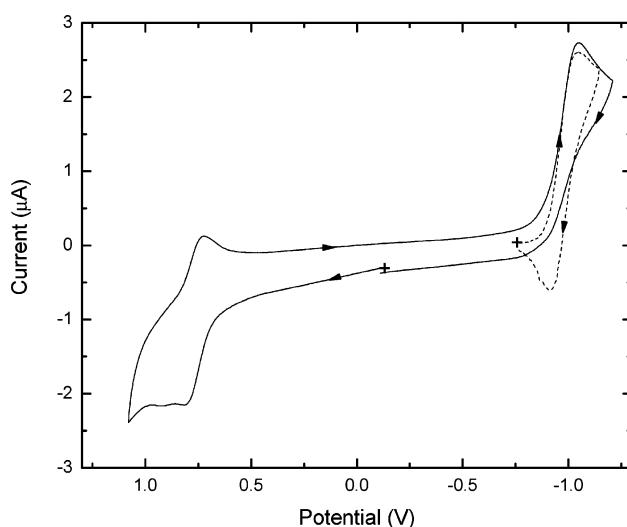


Figure 7. Cyclic voltammograms of a propylene carbonate solution 290 μM in **9** and 0.2 M in TBAP illustrating quasireversible oxidation and reduction. The two scans differ by starting potential (denoted with +), scan direction and scan window. Potentials are versus Fc/Fc⁺.

Importantly, substitution of bpea with strong donor ligands also affords ready access to the $\text{Mn}^{\text{V}}(\text{Mn}^{\text{IV}})_3$ oxidation state. Complexes **4**, **7**, **9**, **10**, and **11** exhibit quasireversible CV for the (V, IV, IV, IV)/(IV, IV, IV, IV) redox couple ($E_{1/2}$ of 0.978, 0.942, 0.775, 0.718, and 0.641 V, respectively), with the R-ida complex **11** having the lowest (V, IV, IV, IV)/(IV, IV, IV, IV) redox couple of the known adamantane-shaped $[\text{Mn}_4\text{O}_6]^{4+}$ complexes. Synthesis, characterization, and reactivity of manganese–oxo complexes in the $\text{Mn}^{\text{V}}(\text{Mn}^{\text{IV}})_3$ oxidation state figure prominently in modeling studies aimed at evaluating recent proposals for PSII-catalyzed water oxidation, in which a Mn^{V} intermediate is proposed for the O–O bond-forming step.^{57–61,114} Furthermore, a $\text{Mn}^{\text{V}}(\text{Mn}^{\text{IV}})_3$ oxidation state has been proposed for the S₄ state of the Mn₄ OEC.^{57, 63, 64}

(113) Manchanda, R.; Brudvig, G. W.; Crabtree, R. H. *Coord. Chem. Rev.* **1995**, *144*, 1–38.

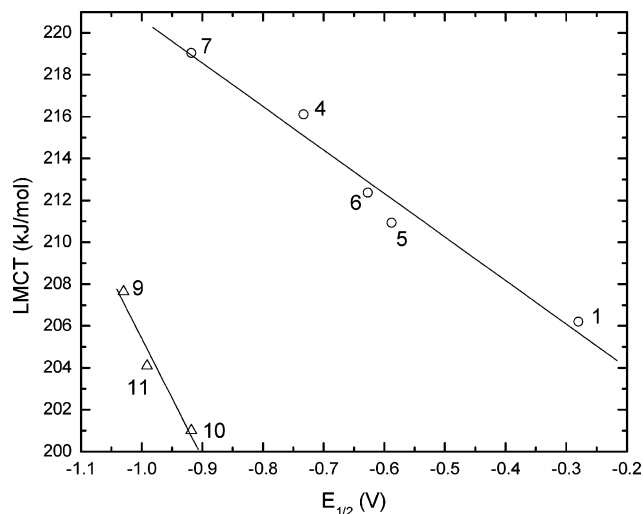


Figure 8. Plot of LMCT energy versus $E_{1/2}$ of the (III,IV,IV,IV)/(IV,IV,IV,IV) redox couple. Δ = iminodicarboxylates and \circ = amines. Potentials are versus Fc/Fc^+ .

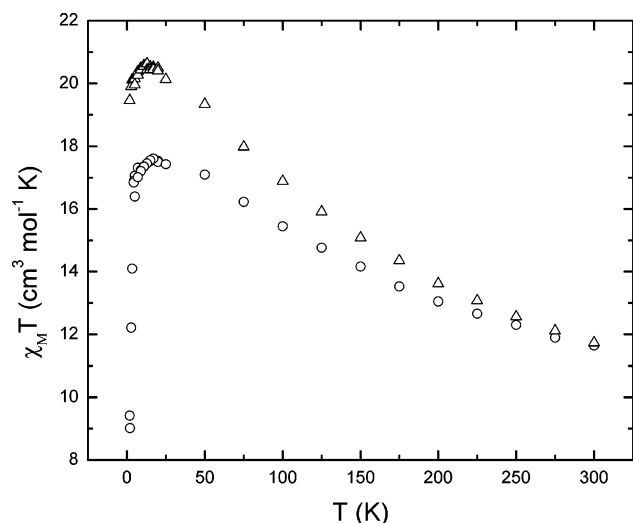


Figure 9. Temperature dependence of $\chi_M T$ of $7(\text{ClO}_4)_4$ (Δ) and **9** (\circ) at 0.5 T.

Magnetic Susceptibility and Isothermal Magnetization.

Magnetic susceptibility measurements versus temperature were conducted on powdered samples of **4**, **7**, **8**, and **9** and isothermal magnetization versus applied magnetic field were measured for **1**, **7**, and **9**.

Magnetic susceptibility data for **7** and **9** are plotted as $\chi_M T$ versus T in Figure 9. Data for **4** and **8** are in Supporting Information as Figures S7 and S8, respectively. Qualitatively, the behavior for adamantane complexes synthesized via ligand substitution is similar to that observed for **1**.^{21,23} Each complex is overall ferromagnetically coupled, with room temperature (300 K) $\chi_M T$ values between 10.9 and 12.3 $\text{cm}^3 \text{mol}^{-1} \text{K}$.¹¹⁵ These values are also similar to the room temperature $\chi_M T$ value for **1** of 10.9. Overall ferromagnetic coupling within **4** has been reported previously.^{19,20} Upon cooling, the value of $\chi_M T$ increases to a maximum in the

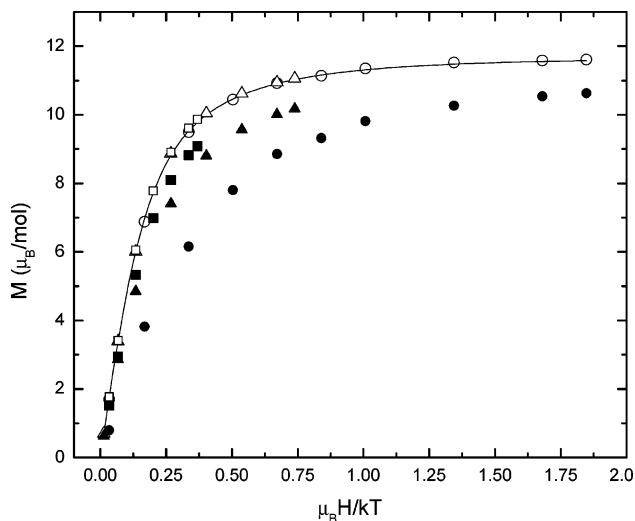


Figure 10. Isothermal magnetization of **7** (\circ , Δ , \square) and **9** (\bullet , \blacktriangle , \blacksquare). The solid line corresponds to a fit of the Brillouin function for $7(\text{ClO}_4)_4$ (2 K data) with $S = 6$ and $g = 1.94$. Symbols: 2 K (\circ , \bullet), 5 K (Δ , \blacktriangle), 10 K (\square , \blacksquare).

vicinity 7–20 K, below which temperature the value decreases. Notable are the maximum $\chi_M T$ values for **4** and **7** at 0.5 T of 20.5 (7 K) and 20.6 (13 K), respectively, which are very close to the value expected for an $S = 6$ ground state of 21.0. It is expected, however, that significant changes in the ligand field environment of the Mn^{IV} ions with ligand substitution, as well as changes in the magnetic exchange pathways due to $[\text{Mn}_4\text{O}_6]^{4+}$ core structural differences for the complexes discussed above might well lead to differences in magnetic exchange and ground-state spin. For example, the values of maximum $\chi_M T$ were highest for the highest symmetry complexes **4** and **7**, somewhat lower for **1** (18.3 at 18 K), and lowest for the mixed ligand complexes **8** and **9** at 17.5 (20 K) and 17.6 (17 K), respectively. Further indications of the differences in the magnetic behavior among these complexes are evident in the variable-field magnetization and analysis of the magnetic susceptibility as a function of temperature.

The ground-state spin of each **1**, **7**, and **9** was studied with isothermal magnetization. The field dependence of the magnetization of **7** at 2, 5, and 10 K, as a plot of M (μ_B/mol) versus $\mu_B H/kT$ (Figure 10), exhibits saturation around 11.6 μ_B/mol , which could be fit with the Brillouin function with $S = 6$ and $g = 1.94$.¹¹⁶ For comparison, analysis of the magnetic behavior of **4** previously established that it has an $S = 6$ ground state.^{19, 20}

On the other hand, the magnetization behavior of **9**, which exhibited saturation around 10.6 μ_B/mol (Figure 10), suggests population of low lying ($S < 6$) states and zero-field splitting of the ground state. The magnetization behavior of **1** (Figure S9) also indicates some degree of zero-field splitting in the ground state.

In prior work, the magnetic susceptibility as a function of temperature for **4** was modeled with the Van Vleck equation¹¹⁷ using an isotropic Heisenberg exchange Hamiltonian

(114) Limburg, J.; Szalai, V. A.; Brudvig, G. W. *J. Chem. Soc., Dalton Trans.* **1999**, 1353–1362.

(115) For comparison, the spin-only $\chi_M T$ value for four uncoupled high-spin d^3 ions is 7.50 $\text{cm}^3 \text{mol}^{-1} \text{K}$.

(116) When H/kT is large, the magnetization M (in units of μ_B/mol) saturates at a value given by gS .

in the form $\hat{H} = -J_{ij}\hat{S}_i\cdot\hat{S}_j$ with a single J (14.5 cm^{-1}), based on an idealized tetrahedral symmetry.²⁰ The quality of the fit, which was relatively poor, was significantly improved with incorporation of a large biquadratic exchange term j ($J = 13.8\text{ cm}^{-1}$, $j = 7.8\text{ cm}^{-1}$). On the other hand, the ferromagnetic exchange of **1**, possessing two different types of oxo bridges coupling the Mn^{IV} ions,²¹ was modeled with $\hat{H} = -J_{ij}\hat{S}_i\cdot\hat{S}_j$ using two exchange constants, giving an excellent fit with $J_1=10.2\text{ cm}^{-1}$, $J_2=90.0\text{ cm}^{-1}$, and $g = 1.88$.²³ A biquadratic exchange term did not improve the quality of the fit markedly. While we have not found a single magnetic exchange model that adequately describes the magnetic behavior of all of the adamantane-shaped $[\text{Mn}_4\text{O}_6]^{4+}$ complexes, the overall ferromagnetic coupling of the Mn^{IV} ions is best regarded as pairwise ferromagnetic. The overall ferromagnetic coupling in these $[\text{Mn}_4\text{O}_6]^{4+}$ cores is unusual among the known tetranuclear manganese–oxo aggregates,^{37,40,42,45,118–124} and is the subject of an ongoing investigation that incorporates broken symmetry/density functional theory (BS/DFT) to model the magnetic exchange.¹²⁵

¹H NMR Spectroscopy. The ¹H NMR spectra of **4–11** can be understood in terms of their magnetic properties and assuming that the solution structural symmetry is the same as that displayed in the solid state. The ¹H NMR spectra of **1**, **7**, **10**, and **11** (Figure 11) are representative of the differences observed for the various types of ligands. ¹H NMR spectra of the remaining complexes can be found in the Supporting Information. Much of the analysis presented here has benefited from earlier research on paramagnetic ¹H NMR properties of manganese–oxo complexes.^{21,25,126,127}

Ligand proton resonances can be separated into two types, those assigned to pyridyl ring protons and those assigned to methylene protons. Proton resonances for the complexes described here are found in the range $+60 > \delta > -152$ ppm and are provided in Table S4. The pyridyl ring proton resonances for **1** are found in the region $+55 > \delta > -20$ ppm, and the methylene groups of **1** fall in the range $-22 > \delta > -82$ ppm.²¹

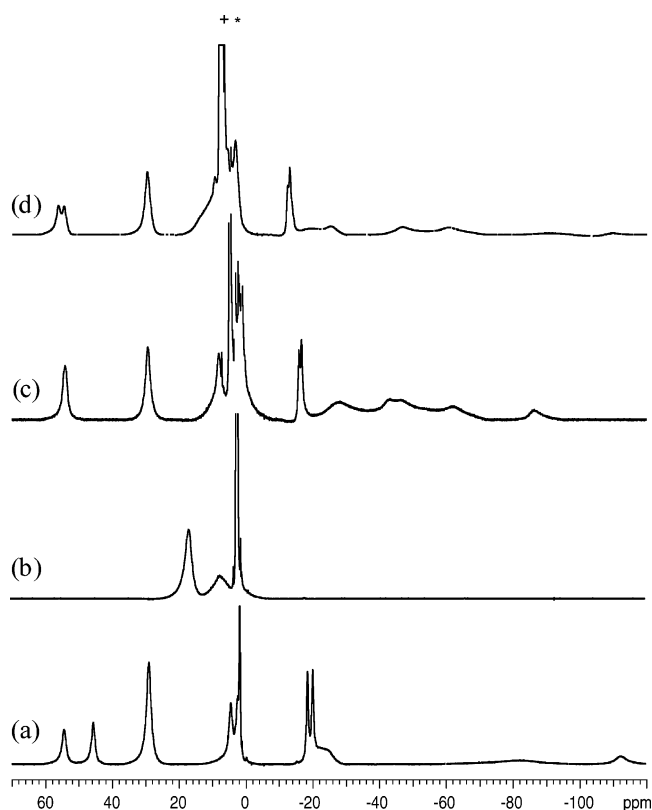


Figure 11. ¹H NMR spectra of (a) **1**, (b) **7**, (c) **10**, and (d) **11**. Conditions: CD_3CN (**1** and **7**), CD_3OD (**10** and **11**). *, CD_2HCN ; +, CD_2HOD .

While the methylene resonances for **4** are at -41.4 ppm (2900 Hz) and -56.7 ppm (1640 Hz), and the methylene resonances of the Medien complex **6** comprise overlapping peaks centered at -45 ppm (3800 Hz), the methylene resonances of the tach complex **7** are downfield at 16.8 ppm (703 Hz) and 7.2 ppm (1640 Hz). The methylene protons of **7** are shifted downfield because they are further removed from the metal center by one additional σ -bond. The methine protons of the tach ligand are not observed for **7**. The two equal-intensity resonances for both **4** and **7** are distinguished by measurably different peak widths. The broader resonances are assigned to those methylene protons directed toward the metal center (axial, H_{ax}), while the sharper resonances are assigned to those methylene protons directed away from the metal center (equatorial, H_{eq}), analogous to the assignments made for the methylene protons of $[\text{Mn}_2\text{O}(\text{OAc})_2(\text{tacn})_2]^{2+}$.¹²⁶

The bpea/R-ida mixed ligand complexes exhibit new resonances in the region $-50 > \delta > -100$ ppm, corresponding to the methylene protons of the R-ida ligands. Additional resonances of some of the alkyl nitrogen substituents are evident in the region $8 > \delta > -1$ ppm. Although the bpea ligands within each of these complexes are equivalent, we did note differences in the split (or lack thereof) of the 4,4' and 5,5' pyridyl ring proton resonances between the complexes.¹²⁸ For example, the 5,5' pyridyl ring proton resonances of **8** and **10** are overlapping at 300 MHz

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(52.0 and 54.7 ppm, respectively), while the splitting of the 4,4' pyridyl ring proton resonances, at -17.0 and -17.3 ppm for **8** and -16.0 and -16.7 for **10**, is 0.3 and 0.7 ppm, respectively. On the other hand, the 5,5' pyridyl ring proton resonances of **11** exhibit a slight split (55.6, 53.8 ppm, $\Delta = 1.8$ ppm), while the splitting of the 4,4' pyridyl ring proton resonances (-16.7 , -17.3 ppm, $\Delta = 0.6$ ppm) is similar to that of **8** and **10**. These data are in contrast to the larger separations of the 4,4' (-18.6 , -20.2 ppm, $\Delta = 1.6$ ppm) and 5,5' (54.9, 46.1 ppm, $\Delta = 8.8$ ppm) pyridyl ring proton resonances of **1**. Previously, we had suggested that the differences in the pyridyl ring proton resonances of **1** were due to longer and shorter Mn–N_{pyr} bonds, the shorter bond leading to tighter coupling to the core and a larger chemical shift.²¹ Comparison of the two Mn–N_{pyr} bonds, 2.090(2) and 2.108(2) Å for **1** (longer – shorter $\Delta = 0.018$ Å) and 2.079(4) and 2.094(4) Å for **11** ($\Delta = 0.015$ Å) shows a similarity of the longer–shorter difference, suggesting that the differences in the 5,5' and 4,4' pyridyl ring proton resonances are due to some other factor. An implication of this result is that although the contact shift of the pyridyl ring proton resonances is likely the dominant component of their isotropic shift, they may have a measurable dipolar component.

Protonation Studies. We have reported structural and electronic changes concomitant with changes in the protonation state of the oxo bridges of **1** and **4**.^{20,21,25} Ligand substitution with iminodicarboxylate ligands greatly increased the overall electron density of the [Mn₄O₆]⁴⁺ cores, as demonstrated by the large shift in reduction potentials of **8**–**11**. Furthermore, the lower symmetry of the aforementioned complexes creates four site-differentiated oxo bridges, compared with two site-differentiated bridging oxo ligands for **1**. Unlike the subtle oxo bridge site differentiation of **1**, however, we expected that the substantial inductive effect of the carboxylate ligands would significantly differentiate oxo bridge electron densities of **8**–**11**. In addition, we anticipated that the increased overall electron density of the [Mn₄O₆]⁴⁺ core would facilitate protonation in water, unlike protonation of **1**, which required a strong acid in acetonitrile.

Reversible protonation of an oxo bridge of **8** in water with HClO₄ to give [Mn₄O₅(OH)(bpea)₂(me-ida)₂](ClO₄) (**8H**-(ClO₄)) was demonstrated spectrophotometrically (Figure 12) and by ¹H NMR in D₂O using CF₃SO₃H to give **8H**(CF₃SO₃) (Figure 13) (see also the ESI mass spectrum of **8**, Figure 5).

Formation of **8H**⁺ was complete after addition of 1 equiv of acid. The observation of distinct ¹H NMR spectra for **8** and **8H**(CF₃SO₃) in the course of titration of **8** with CF₃SO₃H is a consequence of the slow rate of proton self-exchange on the NMR time scale and is consistent with data for other metal–oxo complexes.^{21,25,129–132} The effective

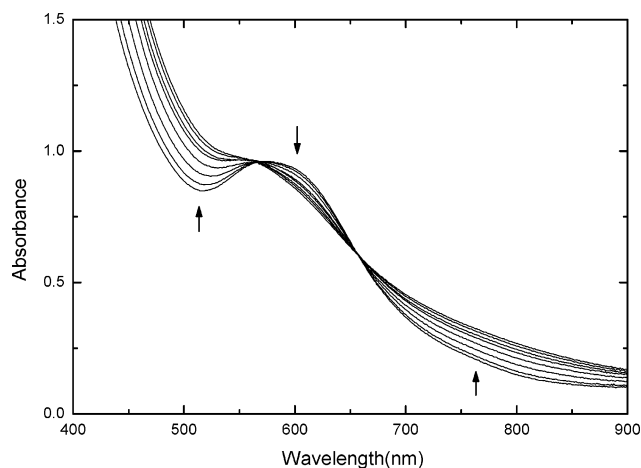


Figure 12. Spectrophotometric titration of an aqueous solution of **8** with HClO₄ (isosbestic points at 567 and 657 nm). See the Experimental Section for details.

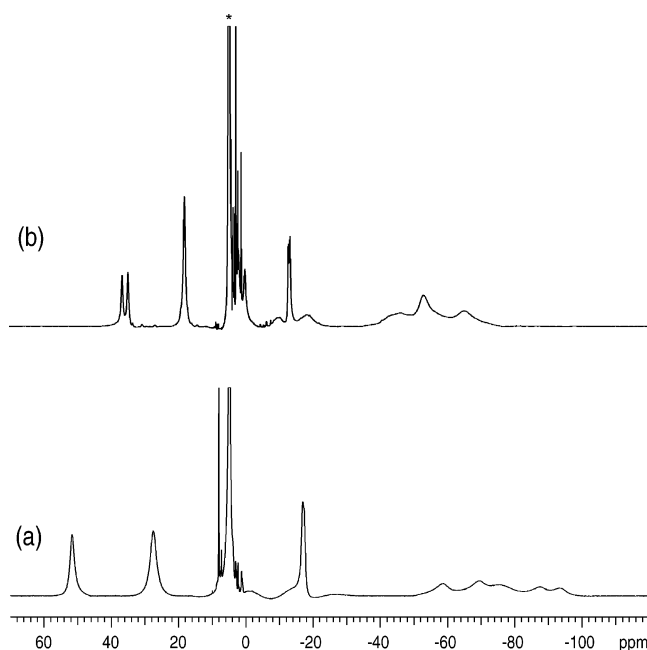


Figure 13. ¹H NMR of (a) **8** and (b) **8** plus 1 equiv of CF₃SO₃H in D₂O to form **8H**(CF₃SO₃). See the Experimental Section for details. *, HOD.

aqueous pK_a of **8** of 2.20 ± 0.03 , determined spectrophotometrically with HClO₄ using eq 1 (Figure S14), is among the highest pK_a values of the adamantane-like [Mn₄O₆]⁴⁺ cores, as expected for the iminodicarboxylate ligand me-ida. Protonation of **8** was also demonstrated with CF₃COOH and CH₃SO₃H, giving an aqueous pK_a of 2.07 and 2.00, respectively. Quantitative reversibility of protonation was verified by spectrophotometric back-titration with Et₃N.

Protonation of **11** in water with HClO₄ and CF₃SO₃H was followed spectrophotometrically as well, and fitting of absorbance versus pH for titration with HClO₄ (Figure S15) gave an aqueous pK_a of 2.32 ± 0.02 . Ligand electronic effects on the adamantane-shaped [Mn₄O₆]⁴⁺ core tune the oxo bridge acidity over 11 orders of magnitude.¹³³ Ligand tuning of the manganese–oxo core effective acidity has also

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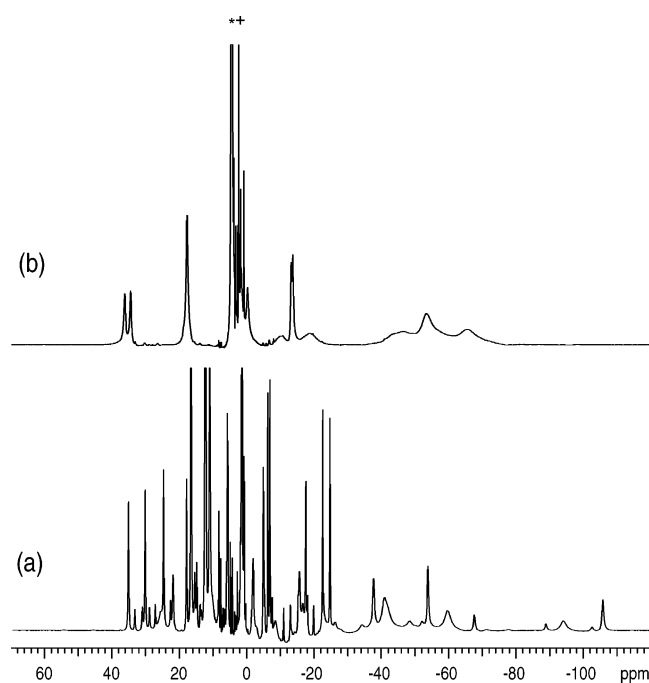
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Table 5. Comparison of Reduction Potentials and Acid Dissociation Constants for **1**, **4**, and **11** with Selected $[\text{Mn}_2\text{O}_2(\text{X-salpn})_2]$ Complexes

	$[\text{Mn}_4\text{O}_6]^{4+}$			$[\text{Mn}_2\text{O}_2]^{4+ a}$	
	$E_{1/2}$ (mV) ^c	$\text{p}K_a$ (H_2O)		$E_{1/2}$ (mV) ^c	$\text{p}K_a$ (H_2O)
1	−280	−6.5 ^d	14 ^b	−440	−0.7 ^d
4	−733	3.10	15 ^b	−795	4.0 ^d
11	−991	2.32	16 ^b	−1048	6.6 ^d

^a $[\text{Mn}_2\text{O}_2]^{4+}$ data from Baldwin et al.¹³⁴ ^b $[\text{Mn}_2\text{O}_2(5\text{-NO}_2\text{-salpn})_2]$ (**14**); $[\text{Mn}_2\text{O}_2(5\text{-Cl-salpn})_2]$ (**15**); $[\text{Mn}_2\text{O}_2(5\text{-OCH}_3\text{-salpn})_2]$ (**16**); X-salpn are derivatives of H_2salpn (*N,N'*-trimethylenebis(salicylidene)-1,3-diaminopropane) with substitution on the phenolate rings. ^c $E_{1/2}$ versus Fc/Fc^+ ; data for **14**, **15**, and **16** corrected to Fc/Fc^+ using $E_{1/2}(\text{Fc}/\text{Fc}^+) = 460$ mV versus the SCE in CH_2Cl_2 with $[\text{Bu}_4\text{N}][\text{PF}_6]$ electrolyte.⁷³ ^d $\text{p}K_a$ measured in acetonitrile. The aqueous $\text{p}K_a$ was estimated using the relation $\text{p}K_a(\text{H}_2\text{O}) = \text{p}K_a(\text{CH}_3\text{CN}) - 7.5$ ¹³⁵

**Figure 14.** ^1H NMR of (a) $1\text{H}(\text{CF}_3\text{SO}_3)_5$ in CD_3CN and (b) $8\text{H}(\text{CF}_3\text{SO}_3)$ in D_2O . *, HOD ; ++, CD_2HCN .

been demonstrated for the dimeric Mn^{IV} series $[\text{Mn}_2(\mu\text{-O})_2(\text{X-salpn})_2]$, whose oxo bridge aqueous $\text{p}K_a$ values ranged from −0.7 to 6.6 (Table 5).¹³⁴

Although the chemical shifts and line widths of the resonances of the protonated complex $8\text{H}(\text{CF}_3\text{SO}_3)$ are qualitatively similar to protonation results observed for **1** in acetonitrile, there are some striking differences (Figure 14). Solution magnetic susceptibility measurements reveal that the magnetic coupling changes from overall ferromagnetic for **8** (χ_{MT} of $12.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) to overall moderate antiferromagnetic for 8H^+ ($6.3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$)¹¹⁵ following

- (133) The highest $\text{p}K_a$ among the $[\text{Mn}_4\text{O}_6]^{4+}$ adamantane cores of 12.5 in acetonitrile for the first protonation of $[\text{Mn}_4\text{O}_6(\text{tame})_4](\text{CF}_3\text{SO}_3)_4$, was determined by spectrophotometric titration with pyridinium triflate in acetonitrile. A corresponding aqueous $\text{p}K_a$ of 5.0 is estimated using the relation $\text{p}K_a(\text{H}_2\text{O}) = \text{p}K_a(\text{CH}_3\text{CN}) - 7.5$ (Kristjansdottir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH Publishers: New York, 1992; pp 309–359) (Dubé, C. E.; Armstrong, W. H. unpublished results).
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protonation with 1 equiv of $\text{CF}_3\text{SO}_3\text{H}$ in D_2O , similar to the degree of change seen for protonation of **1**. However, while there are four site-differentiated oxo bridges in **8**, the solution structural symmetry of 8H^+ reveals essentially a single protonation isomer, unlike the two protonation isomers observed for 1H^+ by ^1H NMR, one for each of the site-differentiated oxo bridges in **1**.^{21,136} Furthermore, 8H^+ exhibits equivalency of the bpea ligands, similar to that observed for **8** (vide supra). The higher solution symmetry of 8H^+ relative to that observed for 1H^+ is consistent with protonation at one of the two oxo bridges on the C_2 axis. We would expect this to be the oxo bridge trans to two carboxylate ligands (atom O(2) in Figure 3), based on the significant donor strength of the carboxylate oxygen atoms.

About 30 min after addition of either $\text{CF}_3\text{SO}_3\text{H}$ or HClO_4 to an aqueous solution of **8** or **11**, the protonated complex precipitated from solution. The precipitate of either 8H^+ or 11H^+ could be readily solubilized with Et_3N , however, affording the spectrum of **8** or **11**, with nearly quantitative recovery.

Concluding Remarks

Although the tetranuclear arrangement of Mn ions in adamantane-shaped $[\text{Mn}_4\text{O}_6]^{4+}$ is too symmetrical and the $\text{Mn}\cdots\text{Mn}$ distance too long for it to be considered as an accurate structural model of the $\text{S}_0\text{--}\text{S}_2$ states of the active site,^{1–6,137} this core has mechanistic implications with regards to S-state advancement and substrate oxidation at the active site. For example, EXAFS analysis of the Mn–oxo core within PSII reveals a metal–metal distance increase observed for the PSII Mn_4 when advancing from S_2 to S_3 states,⁴⁸ suggesting to us that the Mn–oxo core may undergo significant structural rearrangement, rather than necessarily an increase in the Mn– O_{oxo} bond length. We believe a core “shape-shift”, like our recent report of a core rearrangement of a dimer-of-dimers to an adamantane core,⁴³ is a possible explanation for changes in the metal–metal distance observed for advancement from S_2 to S_3 and S_3 to S_0 . We are currently exploring further conditions that promote a core shape-shift from a dimer-of-dimers to an adamantane core, as well as conditions that might promote the rearrangement of an adamantane to a dimer-of-dimers for Mn–oxo adamantanes, such as those reported here.

Although the exact coordination environment is a matter of ongoing investigation, it is generally believed that the Mn–oxo complex of the OEC is coordinated predominantly by carboxylates from aspartate and glutamate, along with oxide bridges and one or two imidazoles.^{8,9,15,16} Substitution reactions of **1** with iminodicarboxylates afforded complexes **8–11** that more closely approximate the coordination environment of PSII and that very likely could not have been

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prepared under the oxidation conditions utilized in self-assembly of high-valent manganese–oxo complexes. Furthermore, the unique substitution chemistry of **1** with R-ida ligands afforded asymmetrically ligated complexes, the mixed ligand nature of which is most likely unachievable using self-assembly synthetic methods.

A special feature of the asymmetrically ligated complexes **8–11** is the substantial site differentiation of the oxo bridges of the $[\text{Mn}_4\text{O}_6]^{4+}$ cores as revealed by protonation. In a number of metalloenzymes, site-specific tuning of the chemical reactivity of the active site is achieved through a combination of coordination of amino acid residues, steric interactions between the metal ions and amino acid residues, and hydrogen bonding. Such factors are difficult to incorporate, however, into structural models of metalloenzymes synthesized by spontaneous self-assembly. Some Mn–oxo dimeric systems have achieved oxo bridge discrimination by the asymmetric coordination of different ligands to the metal ions, as demonstrated in the solid-state structure of $[(\text{Me}_3\text{-tacn})\text{Mn}(\mu\text{-O})_2(\mu\text{-OAc})\text{Mn}(\eta^2\text{-OAc})(\eta^1\text{-OAc})]$ and $[(\text{Me}_3\text{-tacn})\text{Mn}(\mu\text{-O})_2(\mu\text{-OAc})\text{Mn}(\text{bpy})(\text{MeOH})](\text{ClO}_4)_2$ complexes.¹³⁸ In contrast to the subtle oxo bridge site differentiation in **1**, asymmetric ligation of **11** has substantially altered the oxo bridge electron density to afford essentially a single protonation isomer. The differentiated sites within complexes **8–11** using iminodicarboxylate ligation demonstrates how amino acid side chains might similarly differentiate the site of substrate binding within the Mn complex of the OEC.

One of the current proposals for water oxidation suggests that a $\text{Mn}^{\text{V}}=\text{O}$ species^{57–61} may be a key reactive intermediate in the O–O bond-forming step. In this regard, the

electrochemistry of the carboxylate complex **11** is of particular interest, since it has the lowest (V, IV, IV, IV)/(IV, IV, IV, IV) redox couple of the known adamantane-shaped $[\text{Mn}_4\text{O}_6]^{4+}$ complexes and, as such, is an attractive candidate for isolation and reaction studies of stable Mn^{V} –oxo model compounds.

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Supporting Information Available: A description of the synthesis of *N*-cyclopentyliminodiacetic acid, *N*-*tert*-butyliminodiacetic acid, and $(\text{Bu}_4\text{N})_2(\text{me-ida})$; a table of yield, elemental analysis and ^1H NMR data for $(n\text{-Bu}_4\text{N})_2(\text{R-ida})$ and $(n\text{-Et}_4\text{N})_2(\text{R-ida})$; a description of the synthesis of *cis,cis*-1,3,5-triaminocyclohexane; a description of the synthesis of **9** and **10**; tables of yield, elemental analysis, ESI-MS, UV–vis, electrochemistry, IR, and ^1H NMR data for **4–11**; ESI mass spectra of **4–6**, **9–11**; $\chi_{\text{M}}T$ versus *T* plots for **4** and **8**, a *M* ($\mu_{\text{B}}/\text{mol}$) versus $\mu_{\text{B}}H/kT$ plot for **1**; ^1H NMR spectra of **4**, **5**, **6**, and **9**; plots of nonlinear least-squares fit of absorbance versus pH for titration of **8** and **11**; and full crystallographic information for **7** and **11**, including figures illustrating hydrogen bonding. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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