Acknowledgment. We thank the National Science Council of Republic of China and the Croucher Foundation of Hong Kong for support. D.K.P.N. thanks the Croucher Foundation for a studentship.

Registry No. **3a**, 6317-10-8; **3b**, 86201-62-9; **3c**, 77853-39-5; **3d**, 85102-56-3; **3e**, 85102-58-5; **3f**, 113509-22-1; **3g**, 23229-32-5; **3h**, 5425-44-5; **4a**, 4165-81-5; **4b**, 101300-69-0; **4c**, 123751-89-3; (*E*)-**4d**, 123751-90-6; (*Z*)-**4d**, 123751-96-2; (*E*)-**4e**, 123751-91-7; (*Z*)-**4e**, 123751-97-3; **4f**, 123751-92-8; **4g**, 123751-93-9; **4h**, 123751-94-0; **4h′**, 123751-95-1; **4i**, 1450-63-1; **4j**, 20235-61-4; **8a**, 123751-98-4; **8b**, 119946-57-5; **9a**, 123751-99-5; **9b**, 100763-29-9; **11**, 42196-84-9; **12**, 123752-00-1; **13**, 123752-01-2; **14a**, 1432-53-7; **14b**, 123752-02-3; $NiCl_2(PPh_3)_2$, 14264-16-5; cyclopropylmagnesium bromide, 23719-80-4; (*E*)-2-butylcyclopropylmagnesium bromide, 123752-03-4; (*Z*)-2-butylcyclopropylmagnesium bromide, 123752-04-5; 2,2-diphenylcyclopropylmagnesium bromide, 123752-05-6; bicyclo[4.1.0]heptan-7-ylmagnesium bromide, 123752-06-7; cyclobutylmagnesium bromide, 13384-48-0.

Supplementary Material Available: Physical data (IR, NMR, mp) of dienes and related compounds (3 pages). Ordering information is given on any current masthead page.

A Novel Tetranuclear Manganese Complex That Displays Multiple High-Potential Redox Processes. Synthesis, Structure, and Properties of $\{[Mn_2(TPHPN)(O_2CCH_3)(H_2O)]_2O\}(ClO_4)_4\cdot 2CH_3OH$[1]

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As the primary source of atmospheric dioxygen, photosynthetic water oxidation is an essential process for aerobic organisms. This four-electron, four-proton reaction occurs at the photosystem II oxygen-evolving complex (PSII OEC) in green plants and algae. While it is known that four manganese atoms per PSII OEC are required for optimal oxygen evolution activity, there is no consensus as to the precise arrangement of the Mn atoms, nor is the mechanism of water oxidation well understood.[2] One prevalent notion is that the manganese center functions to store four oxidizing equivalents at an electrochemical potential high enough (≥0.8 V vs NHE at pH = 7) to carry out the oxidation of water to dioxygen.[3] It is thought that two water molecules (or deprotonated derivatives thereof) may be transformed to dioxygen by a concerted single oxidative process. In the Kok S-state scheme for the PSII OEC catalytic cycle,[4] this four-electron process would occur between the S_4 and S_0 states. Within this conceptual framework, it is clear that one criterion for a functional synthetic analogue is that it should exhibit four high-potential redox processes. Several high-valent tetranuclear species have been reported;[5-8] however, judging by conclusions from recent XAS measurements on oriented samples of PSII OEC,[2e] none of these model complexes are structurally congruent with the native manganese aggregate, nor has it been reported that any of them, or any other polynuclear manganese complexes for that matter, exhibit multiple redox processes at high potential. In this report we describe the synthesis and structure of a novel mixed-valence $[Mn^{II}_2Mn^{III}_2]$ tetranuclear complex, $\{[Mn_2(TPHPN)(O_2CCH_3)(H_2O)]_2O\}(ClO_4)_4$ (**1**), which does indeed display several quasireversible oxidations between 0.8 and 1.4 V vs SSCE. Furthermore, complex **1** is the first high-valent tetranuclear species

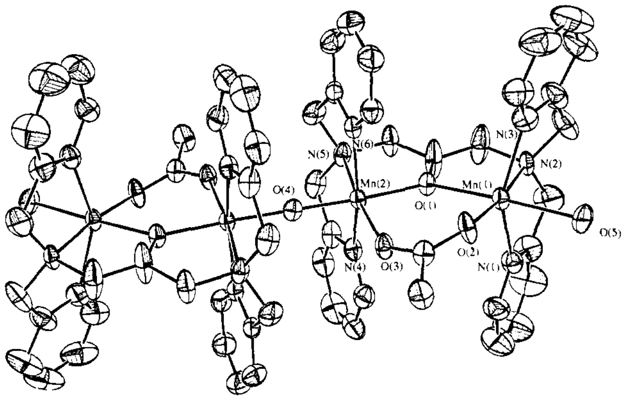

Figure 1. Structure of $\{[Mn_2(TPHPN)(O_2CCH_3)(H_2O)]_2O\}^{4+}$ (**1**) showing the 40% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms are omitted for clarity. Unlabeled atoms are related to labeled ones by an inversion center. Selected interatomic distances (Å) and angles (deg) are as follows: Mn(1)–O(1), 2.148 (3); Mn(1)–O(2), 2.097 (3); Mn(1)–O(5), 2.174 (3); Mn(1)–N(1), 2.248 (5); Mn(1)–N(2), 2.281 (4); Mn(1)–N(3), 2.246 (5); Mn(2)–O(1), 1.921 (3); Mn(2)–O(4), 1.766 (1); Mn(2)–O(3), 2.096 (3); Mn(2)–N(4), 2.097 (4); Mn(2)–N(5), 2.238 (4); Mn(2)–N(6), 2.092 (4); Mn(1)···Mn(2), 3.689 (1); Mn(2)···Mn(2′), 3.532 (1); Mn(2)–O(4)–Mn(2′), 180.0; Mn(1)–O(1)–Mn(2), 130.0 (2); O(1)–Mn(1)–O(5), 173.7 (1); O(1)–Mn(2)–O(4), 175.5 (1).

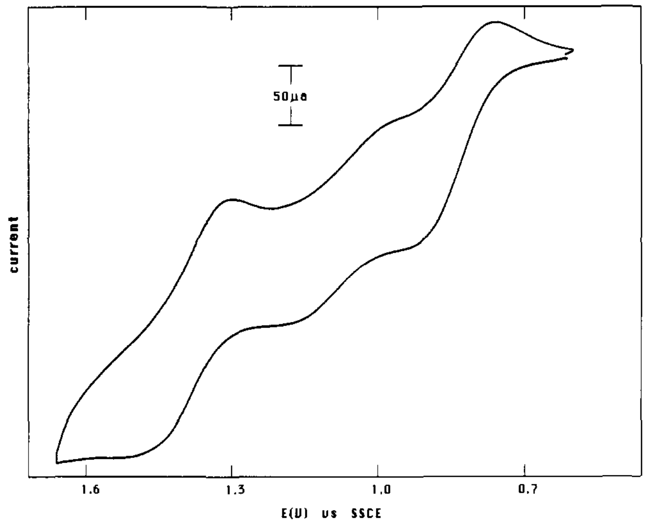

Figure 2. Cyclic voltammogram of **1** in CH_3CN using 0.1 M Et_4NClO_4 as supporting electrolyte, a Pt working electrode, a Pt wire counter electrode, an SSCE reference electrode, and a scan speed of 50 mV/s.

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[1] Abbreviations used: HTPHPN, *N,N,N′,N′*-tetrakis(2-pyridylmethyl)-2-hydroxypropane-1,3-diamine; PSII OEC, photosystem II oxygen-evolving complex; XAS, X-ray absorption spectroscopy; SSCE, saturated sodium calomel electrode; $HBpz_3$, hydrotris(1-pyrazolyl)borate; tacn, 1,4,7-triazacyclononane; bpy, 2,2′-bipyridine; L-Im, 2,6-bis[[[bis(1-methylimidazol-2-yl)methyl]amino]methyl]-4-methylphenol; Him, imidazole.

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that contains coordinated H_2O molecules.

To the best of our knowledge, metal complexes with the septadentate ligand used in this work have not been reported previously. Compound **1** was prepared as follows. To a solution containing 0.227 g (0.500 mmol) of HTPHPN,[9] 0.0495 g (0.489 mmol) of Et_3N, and 20 mL of MeOH was added 0.268 g (1.00 mmol) of $Mn(O_2CCH_3)_3\cdot 2H_2O$ followed by 0.281 g (2.00 mmol) of $NaClO_4\cdot H_2O$. After being stirred overnight, the solution was concentrated by evaporation. The green crystalline solid that precipitated (0.152 g, 34.6% yield) over several days was analytically pure,[10] and from this material was selected a single crystal for X-ray diffraction studies.[11]

The structure of **1**, shown in Figure 1, consists of a pair of $Mn^{II}Mn^{III}$ complexes linked by a single oxo bridge between the Mn^{III} ions. Trapped valence is clearly indicated as bond distances to Mn(1) are as expected for Mn^{II} and likewise Mn(2) can be assigned as the Mn^{III} ion. Compound **1** represents the first example of a structurally characterized species containing two Mn^{III} ions linked only by a linear oxo bridge and coordinated by biologically relevant donors. The Mn^{III}–O_{oxo} bond distance in **1** is comparable to the corresponding distances in $[Mn_2O(O_2CCH_3)_2L_2]^{n+}$ (L = $HBpz_3$, $n = 0$;[12] L = tacn, $n = 2$[13]) and $[Mn_2O(O_2CCH_3)_2(H_2O)_2(bpy)_2]^{2+}$ (**2**).[14] There are two short and one long Mn–N bond distances to Mn(2), indicating that elongation occurs along the O(3)–Mn(2)–N(5) axis. This sort of deviation from octahedral symmetry, resulting from expected Jahn–Teller distortions for high-spin d^4 ions, is common among Mn(III) complexes. The Mn(1)–OH_2 distance in **1** is 0.14 Å shorter than the average Mn–OH_2 distance in **2**,[14] because in the latter complex the OH_2 molecule lies along a Jahn–Teller elongated axis. A notable feature in the structure of **1** is that the tridentate N_3 ends of the TPHPN ligand bind in a meridional fashion. In marked contrast, the N_3 tripods of related septadentate and hexadentate ligands bind facially in several binuclear and tetranuclear Mn[15-17] and Fe[18,19] complexes. The Mn(1)–Mn(2) distance in **1** (3.689 (1) Å) is somewhat longer than corresponding distances in triply bridged $Mn^{II}Mn^{III}$ complexes $[Mn_2(bpmp)(O_2CCH_3)_2]^{2+}$ (3.447 (1) Å)[16] and $[Mn_2(LIm)(O_2CCH_3)_2]^{2+}$ (**3**) (3.54 (1) Å).[15]

Susceptibility measurements of a powdered sample of **1** indicate that the magnetic moment per molecule decreases from 8.7 μ_B at 279 K to 6.8 μ_B at 6.0 K. Considering that the magnetic moment per molecule would be 10.86 μ_B ($2 \times Mn^{II} + 2 \times Mn^{III}$) in the limit of no interionic magnetic coupling, it is evident that antiferromagnetic interactions within the aggregate are operative. This magnetic behavior is consistent with relatively weak antiferromagnetic interactions between Mn^{II} and Mn^{III} atoms, as observed for several $Mn^{II}Mn^{III}$ binuclear species,[15-17,20] and moderately strong antiferromagnetic coupling between Mn^{III} ions, as observed for a binuclear complex in this laboratory.[21] A detailed account of the magnetic properties of **1** will be reported elsewhere.

From the viewpoint of attempting to mimic the PSII OEC manganese aggregate, the electrochemical properties are perhaps of greatest interest. The cyclic voltammogram of **1**, measured in CH_3CN solution, is displayed in Figure 2. Three quasireversible redox waves with $E_{1/2}$ values of approximately 0.83, 1.05, and 1.35 V vs SSCE are evident. When an electrode was poised at 0.5 V (vs SSCE) in a MeCN solution of **1**, very little current passed and no UV–vis spectral changes occurred, while at higher voltages, distinct spectral changes were observed. Thus the cyclic voltammetric waves can be assigned tentatively as shown below, although oxidation of coordinated H_2O cannot be ruled out.

$$(\mathrm{II,III,III,II}) \xrightleftharpoons{0.83\ \mathrm{V}} (\mathrm{II,III,III,III}) \xrightleftharpoons{1.03\ \mathrm{V}} (\mathrm{III,III,III,III}) \xrightleftharpoons{1.35\ \mathrm{V}} (\mathrm{III,III,III,IV})$$

The separation between the first two oxidation processes in **1** (~0.2 V) is substantially less than in several binuclear species that exhibit two redox processes: **3**($\Delta E_{1/2} = 0.58$ V),[15] $[Mn_2O_2(tren)_2]^{3+}$ ($\Delta E_{1/2} = 0.8$ V),[22] $[Mn_2O_2(phen)_4]^{3+}$ ($\Delta E_{1/2} = 1.0$ V).[23] This may be a result of the weak interaction between the two Mn^{II} ions oxidized in the proposed first two cyclic voltammetric processes for **1**. In the PSII OEC modeling context discussed above, this result suggests that one strategy that may be employed to group oxidations closely together is to ensure that not all four of the manganese atoms be too closely coupled to one another. Multiple redox waves at high potential have not been reported for more compact tetranuclear complexes such as $[Mn_4O_6(tacn)_4]^{4+}$,[6] $[Mn_4O_2(O_2CCH_3)(bpy)_2]^{1+}$,[7a] $[Mn_4O_2(O_2CCH_3)_6(bpy)_2]$,[7b] $[Mn_4O_2(O_2CCPh_3)_6(OEt_2)_2]$,[5] and $[Mn_4O_3Cl_6(HIm)(OAc)_3]^{2-}$.[8]

In summary, a novel tetranuclear complex (**1**) with an average manganese oxidation state of +2.5 has been discovered. The magnetic properties of this species are as expected on the basis of data recently reported for binuclear $Mn^{II}Mn^{III}$ and $Mn^{III}Mn^{III}$ compounds. Compound **1** is the first crystallographically characterized high-valent tetranuclear manganese complex that has coordinated water molecules. Most importantly, **1** has several oxidation waves that are of sufficiently high potential to carry out water oxidation. The reactivity properties of **1** and related species are being examined.

Note Added in Proof. Compound **1**, as a triflate salt, has just been reported: Suzuki, M.; Sugisawa, T.; Senda, H.; Oshio, H.; Uehara, A. *Chem. Lett.* **1989**, 1091–1094.

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Registry No. 1, 123053-98-5; **1**·CH_3OH, 123122-67-8; $\{[Mn_2(TPHPN)(O_2CCH_3)(H_2O)]_2O\}^{5+}$, 123053-99-6; $\{[Mn_2(TPHPN)(O_2CCH_3)(H_2O)]_2O\}^{6+}$, 123054-00-2; $\{[Mn_2(TPHPN)(O_2CCH_3)(H_2O)]_2O\}^{7+}$, 123054-01-3.

Supplementary Material Available: Atomic positional and thermal parameters and intramolecular distances and angles for $\{[Mn_2(TPHPN)(O_2CCH_3)(H_2O)]_2O\}(ClO_4)_4\cdot 2CH_3OH$ (12 pages). Ordering information is given on any current masthead page.

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(9) The septadentate ligand HTPHPN was prepared by alkylation of 2-hydroxy-1,3-diaminopropane with 2-(chloromethyl)pyridine.

(10) Elemental analysis of **1**. Calcd for $C_{60}H_{76}Cl_4Mn_4N_{12}O_{27}$: C, 40.97; H, 4.35; Mn, 12.50; N, 9.56. Found: C, 41.24; H, 4.24; Mn, 12.10; N, 9.58.

(11) X-ray analysis: Compound **1** crystallizes in the monoclinic space group $P2_1/n$, with $a = 12.527$ (2) Å, $b = 21.098$ (5) Å, $c = 13.953$ (3) Å, $\beta = 90.19$ (2)°, $V = 3688$ (2) Å^3, $\rho_{calcd} = 1.58$ g cm^{-3}, and $Z = 2$. Data collection at 165 K out to 50° in 2θ provided 4735 reflections with $I > 3\sigma(I)$. The structure was solved by direct methods (SHELXS 86) and refined by using 511 parameters to final R (R_w) values of 4.91% (6.94%).

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