erman,[20a] dimethyl 2-oxopentylphosphonate[30] (388 mg, 2 mmol) in 2 mL of THF was added to a rapidly stirred suspension of sodium hydride (45.6 mg, 1.9 mmol) in THF (5 mL) at −10 °C. The resulting suspension was stirred at −10 °C for 30 min, and then **44a** (229 mg, 1 mmol) in THF (5 mL) was added over 5 min. After stirring an additional 10 min at −10 °C, the mixture was allowed to warm to room temperature and then refluxed for 1 h. The reaction mixture was partitioned between ether (20 mL) and 1 M NaOH (10 mL), after which the aqueous layer was washed with ether (20 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. Chromatography on silica gel (EtOAc–hexane, 1:1) gave **44b** (278 mg, 90%) as a colorless solid. Recrystallization from ether–hexane (3:7) gave colorless needles: mp 74–75 °C; IR (KBr) 2.94, 5.86, 6.05, 6.66 μm; ^{1}H NMR δ 0.81 (d, 3 H, J = 6.4 Hz), 0.90 (t, 3 H, J = 7.3 Hz), 0.98–1.84 (m, 9 H, 1.43, overlapping singlet, 9 H), 2.02 (br t, 1 H), 2.53 (t, 2 H, J = 7 Hz), 3.94 (br m, 1 H), 4.74 (br d, 1 H), 6.08 (d, 1 H, J = 16 Hz), 6.68 (dd, 1 H, J = 16, 9 Hz); $[\alpha]^{24}_{D}$ +53.2° (c 0.43, $CHCl_3$); chemical ionization mass spectrum, m/z (rel intensity) M + 1 (22), 209 (100), 265 (26). Anal. Calcd for $C_{18}H_{30}NO_3$: C, 70.10; H, 9.80. Found: C, 69.93; H, 9.65.

(+)-Pumiliotoxin C (45). A solution of **44b** (145 mg, 0.47 mmol) in 2 mL of ethanol was treated with hydrogen (1 atm) in the presence of 5% palladium carbon (20 mg) until the theoretical amount of hydrogen was absorbed. The catalyst was removed by filtration through Celite, and the resulting solution was concentrated. The residue was treated with 1 mL of 90% trifluoroacetic acid (TFA) at room temperature for 1 h. After removal of the excess TFA under reduced pressure, the residue was made basic with 1 N NaOH and washed with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated to give the $\Delta^{1,2}$ imine, which was immediately dissolved in 5 mL of ethanol and several drops of concentrated HCl solution. Hydrogenation in the presence of 5% palladium on carbon (50 mg) for 6 h, removal of the catalyst by filtration through Celite, and concentration gave essentially pure (+)-pumiliotoxin C (109 mg, 72%) as the amine hydrochloride. Recrystallization from 2-propanol afforded the hydrochloride as colorless needles: mp 285–286 °C (sealed capillary); lit. mp 286–288 °C; ^{1}H NMR δ ($CDCl_3$) 0.87 (d, 3 H), 0.89 (t, 3 H), 0.90–2.54 (m, 16 H), 2.98 (br m, 1 H), 3.32 (br d, 1 H), 8.46 (br m, 1 H), 9.62 (br m, 1 H); ^{13}C NMR ($CDCl_3$) δ 60.2, 58.2, 41.1, 35.0, 34.5, 29.2, 27.3, 25.3, 23.3, 20.6, 19.7, 19.2, 13.7; $[\alpha]^{24}_{D}$ +16.1°, $[\alpha]^{24}_{435}$ +28.8° (c 0.50, MeOH); lit. $[\alpha]^{20}_{D}$ +16.4°, $[\alpha]^{20}_{436}$ 28.1° (c 1.00, MeOH); chemical ionization mass spectrum, m/z (rel intensity) 194 (100), 152 (88). The spectral data were in agreement with those reported for the natural product.[28]

Acknowledgment. This work was supported by the National Institute of General Medical Science (GM-33061). We thank Professor Overman for a generous sample of **46**, Dr. R. K. Kullnig for X-ray diffraction analyses of **5** and **18**, and the National Science Foundation for funds for purchase of the Nicolet X-ray diffractometer used in this study. Address correspondence concerning the X-ray analyses to Dr. Rudolph K. Kullnig, Department of Chemistry, RPI. We thank Degussa AG for a generous gift of L-proline.

Supplementary Material Available: Tables of crystal structure data, atomic coordinates, bond lengths, bond angles, anisotropic parameters, and hydrogen atom coordinates for **5** and **18** (6 pages). Ordering information is given on any current masthead page.

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[30] Prepared from methyl butyrate by the procedure described in Corey, E. J.; Kwiatkowski, G. T. *J. Am. Chem. Soc.* **1966**, *88*, 5653.

Communications to the Editor

Modelling the Photosynthetic Water Oxidation Center: Preparation and Physical Properties of a Tetranuclear Oxide Bridged Mn Complex Corresponding to the Native S_2 State

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Elucidating the precise structure and mode of action of the Mn aggregate responsible for photosynthetic water oxidation/oxygen evolution represents an area of intense research at the present time. It is generally believed that four Mn atoms per photosystem II (PS II) reaction center are essential for activity.[2] The Mn aggregate is capable of cycling between five oxidation levels (S_0–S_4) during the catalytic cycle[3] but can also adopt an additional "super-reduced" oxidation level, labeled S_{-1}, under certain conditions.[4] We have been seeking inorganic model complexes of this biological unit to assist in elucidation of the precise structural changes and concomitant substrate transformations during turnover. We recently reported the synthesis of complexes containing the $[Mn_4O_2]$ core with structural features similar to the enzyme and isolable in three oxidation levels corresponding to the native S_{-1}, S_0, and S_1 levels.[5] Since the EPR active S_2 level has allowed the most detailed study of the biological unit to date, we have turned our attention to the synthesis of an Mn_4 complex in this important oxidation level (3 Mn^{III}, Mn^{IV}) and herein report the successful attainment of this objective.

A stirred slurry of brown "manganic acetate" (0.54 g)[6] in degassed MeCN (25 mL) was treated dropwise with Me_3SiCl (0.66 mL). To the resulting solution was added imidazole (HIm, 0.25 g) in MeCN (15 mL), followed by $NaClO_4$ (0.29 g) in MeCN (10 mL). The final red-brown solution was stirred for a further 10 min, filtered, and left undisturbed for 2 days at ambient temperature. The resulting dark brown crystals were collected by filtration, washed with MeCN, and dried; yield ~ 20%. The product was identified by analysis[7] and crystallographic

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[1] (a) Indiana University, Chemistry Department. (b) Indiana University, Molecular Structure Center. (c) University of Illinois.

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[6] Prepared by a slight modification to the standard reaction of Mn(OAc)$_2$ with $KMnO_4$ in hot glacial acetic acid, as described by Lis, T. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2042. Full details, together with a more detailed discussion of the preparation of **1**, will be provided in the full report of this work.

[7] Anal. Calcd for $C_{18}H_{27.5}N_{7.5}O_9Cl_6Mn_4$: C, 23.36; H, 3.00; N, 11.35; Cl, 22.98; Mn, 23.75. Found: C, 22.96; H, 3.06; N, 11.48; Cl, 22.98; Mn, 23.17.

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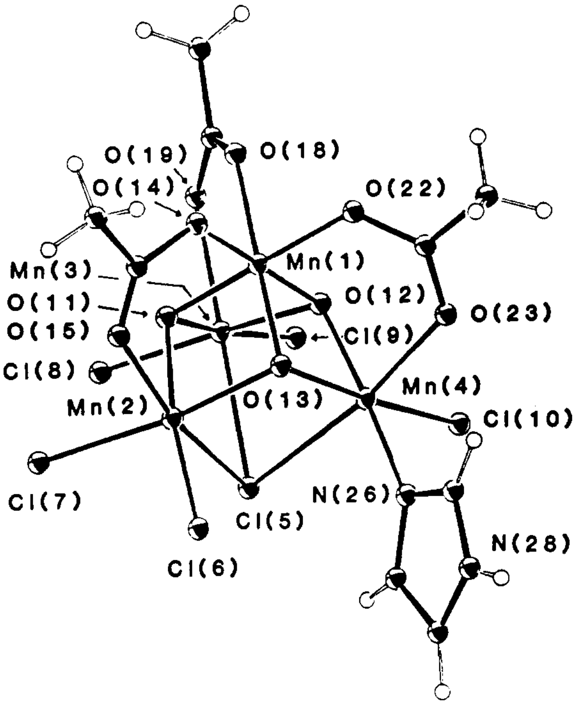

Figure 1. The structure of the anion of **1** showing the labeling scheme. Selected bond distances (Å) are as follows: Mn(1)···Mn(2), 2.818 (4); Mn(1)···Mn(3), 2.818 (5); Mn(1)···Mn(4), 2.806 (5); Mn(2)···Mn(3), 3.323(5); Mn(2)···Mn(4), 3.285 (5); Mn(3)···Mn(4), 3.246 (5); Mn(1)–O(11), 1.844 (13); Mn(1)–O(12), 1.858 (14); Mn(1)–O(13), 1.797 (13); Mn(2)–O(11), 1.962 (13); Mn(2)–O(13), 1.955 (12); Mn(3)–O(11), 1.999 (14); Mn(3)–O(12), 2.002 (14); Mn(4)–O(12), 1.885 (13); Mn(4)–O(13), 1.977 (13); Cl(5)–Mn(2,3,4), 2.630 (7), 2.633 (6), 2.608 (7); Mn(1)–O(14,18,22), 1.950 (14), 1.958 (13), 1.958 (15); Mn(2)–O(15), 2.212 (14); Mn(3)–O(19), 2.198 (15); Mn(4)–O(23), 2.144 (14); Mn(2)–Cl(6,7), 2.251 (6), 2.263 (6); Mn(3)–Cl(8,9), 2.264 (7), 2.270 (7); Mn(4)–Cl(10), 2.280 (7); Mn(4)–N(26), 1.978 (16).

means[8] to be $(H_2Im)_2[Mn_4O_3Cl_6(HIm)(OAc)_3]\cdot 1.5MeCN$ (**1**; H_2Im^+ = imidazolium cation). The structure of the anion of **1** is shown in Figure 1. The central $[Mn_4(\mu_3\text{-}O)_3(\mu_3\text{-}Cl)]^{6+}$ core is best considered as a Mn_4 pyramid with Mn(1) at the apex, μ_3-Cl atom Cl(5) bridging the basal plane, and a μ_3-O bridging each of the remaining three faces; alternatively, the core can be described as a severely distorted Mn_4O_3Cl cubane. A bridging AcO^- across each Mn(1)–Mn(2,3,4) edge, five terminal Cl atoms, and a terminal HIm group complete distorted octahedral Mn coordination. The unique HIm ligand destroys idealized C_{3v} symmetry. Mn···Mn separations fall into two types; Mn(1)···Mn(2,3,4) (av. 2.814 Å) are distinctly shorter than those between basal Mn atoms (av. 3.285 Å), consistent with the differing bridging modes. Charge considerations necessitate a mixed-valence $Mn_3^{III}Mn^{IV}$ description,[9] and, based on metal–ligand bond distances, Mn(1) is assigned as the Mn^{IV} center.

The solid-state magnetochemistry of **1** is intriguing. The effective magnetic moment (μ_{eff}) per molecule increases gradually with decreasing temperature from 8.82 μ_B at 300.0 K to a maximum of 9.54 μ_B at 60 K, below which μ_{eff} decreases to 7.16 μ_B at 5.0 K. These data are qualitatively in agreement at this stage with the model proposed by de Paula et al.[10] for the native S_2 state.

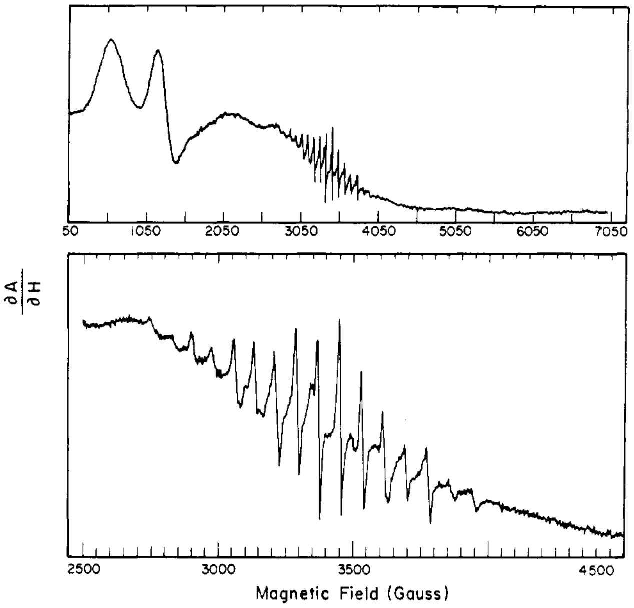

Figure 2. X-band EPR spectrum of complex **1** in a DMF/toluene glass at 60 K and an expansion of the $g = 2$ region.

In this model, the S_2 state consists of an aggregate comprising two inequivalent pairs of Mn ions. The $Mn^{IV}Mn^{III}$ pair is strongly antiferromagnetically coupled to give an $S = 1/2$ state which is ferromagnetically coupled to the $Mn^{III}Mn^{III}$ pair, the latter being itself weakly antiferromagnetically coupled. The observed increase in μ_{eff}/molecule as the temperature is decreased from 300 to 60 K might reflect the ferromagnetic interaction between the two Mn ion pairs. Exact values of the magnetic exchange parameters for **1**, however, are the objectives of detailed analysis of the susceptibility and EPR data currently in progress.

X-band EPR spectra (3.8–90 K) were run for microcrystalline **1** and for a DMF/toluene glass of **1**. The powder spectra are relatively uninformative (broad $g \approx 2$ and $g \approx 4$ signals), presumably due to spin–spin relaxation. As can be seen in Figure 2, however, the glass EPR spectrum exhibits considerable fine and manganese hyperfine structure. This 60 K spectrum displays two low-field transitions at ~500 and ~1250 G as well as a hyperfine-structured signal centered at ~3300 G. Experiments at frequencies other than X-band are underway to understand this fine structure. It is interesting that the intensity and resolution of the hyperfine-structured signal at $g \approx 2$ are maximized at ~60 K, the temperature at which μ_{eff}/molecule undergoes a maximum. Some support for the fact that the spectrum shown in Figure 2 is that for the tetranuclear complex **1** can be drawn from the similarity of this spectrum to the 7.5 K spectrum obtained from an analogous, structurally characterized, *uncharged* $Mn^{IV}Mn_3^{III}$ complex[10] in noncoordinating CH_2Cl_2/toluene glass; experiments are underway to further eliminate the possibility that **1** breaks into two binuclear complexes in DMF/toluene and that one or both give rise to the EPR signal shown in Figure 2. The Mn hyperfine structured $g \sim 2$ signal seen in the spectrum of **1** is due to molecules in an $S = 1/2$ state. Some 16 Mn hyperfine lines can be seen on this $g \sim 2$ signal, whereas 17–19 Mn hyperfine lines have been reported[11,12] for the $g = 2$ signal of the S_2 state of PSII. The intensity pattern of the 16-line signal of **1** (Figure 2) is in keeping with appreciable hyperfine coupling to only two Mn ions, each with a different hyperfine-coupling constant. A more detailed EPR and ENDOR examination of this molecule is in progress.

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(8) Crystallographic data at −158 °C: orthorhombic, space group *Pbca*; $a = 14.307$ (14) Å, $b = 14.668$ (14) Å, $c = 31.319$ (36) Å, $Z = 4$; $R = 0.0810$, $R_w = 0.0870$; using 2513 unique intensities with $I > 2.33\sigma(I)$. All non-hydrogen atoms were refined anisotropically except the disordered MeCN molecules. Only hydrogen atoms of the anion, included as fixed atom contributors, were used in the final refinement cycles.

(9) The average metal oxidation state of +3.25 was confirmed by a standard iodimetric redox titration which gave a value of +3.23 ± 0.03.

(10) The complex is $Mn_4O_3Cl_4(OAc)_3(py)_3$; its EPR spectrum in a CH_2Cl_2/toluene glass also displays the two low-field fine structure features and a hyperfine-structured feature at $g \sim 2$: Vincent, J. B.; Christou, G.; Chang, H.-R.; Li, O.; Hendrickson, D. N., work in progress. Complex **1** is insoluble in CH_2Cl_2.

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In summary, a potential model of the important S_2 state of the oxygen evolution enzyme has been obtained, based on the following similarities with the latter: (i) a metal nuclearity of four and the presence of oxide bridges; (ii) an average metal oxidation state of +3.25; (iii) two types of inequivalent Mn atoms; (iv) both "short" (av 2.814 Å) and "long" (av 3.285 Å) Mn···Mn separations (EXAFS data on S_1 indicate corresponding values of 2.69 (3) and ~3.3 Å[3b,13]); (v) observed spin states and hyperfine EPR features consistent with those of the native site.

Finally, terminal Mn–Cl linkages (av 2.266 Å) are not to be found in the native unit based on available data, and attempts to remove them from **1** are in progress, but whether a μ_3-Cl as found in **1** might be present is uncertain, especially given the long bond lengths (av 2.624 Å) which might make its spectroscopic identification more difficult. It is thus tempting to speculate whether such a μ_3-bridging requirement in some S_n states of the native system might be the origin of the recognized "Cl-dependence" of oxygen evolution.[14] Further studies are in progress, and additional Mn_4 species at this oxidation level are under characterization.[10,15]

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Supplementary Material Available: Fractional coordinates and isotropic and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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Organodiiron "Electron Reservoir" Complexes Containing a Polyaromatic Ligand: Syntheses, Stabilization, Delocalized Mixed Valences, and Intramolecular Coupling

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Transition-metal complexes with stable redox series have attracted attention recently because of their potential applications to technological devices.[1] Mononuclear organoiron sandwiches have already disclosed properties of electron-transfer (ET) catalysts.[2] We now report a novel series of diiron complexes of polyaromatics which can be reduced either in four single-electron steps or in a single two-electron step depending on the stereoelectronic design of the ligands. Also included are the first spectroscopic and structural characteristics of the bicyclohexadienylidene ligand.

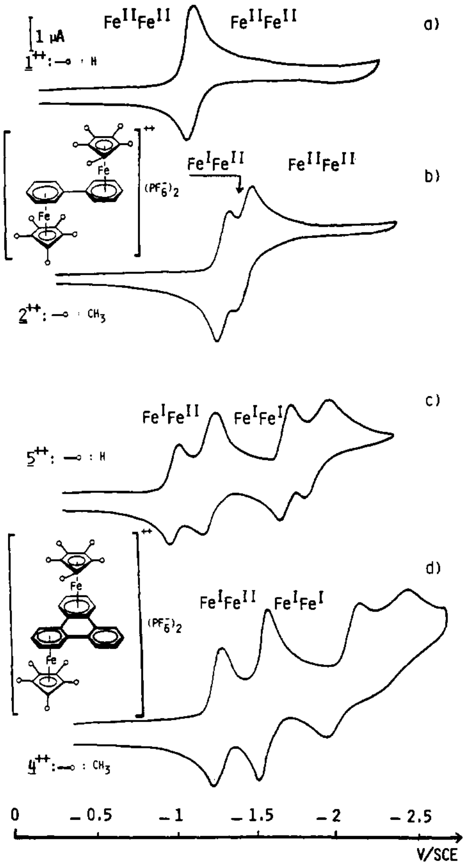

Figure 1. CV of the dicationic diiron complexes of biphenyl [(a) Cp, $\mathbf{1}^{2+}$; (b) Cp*, $\mathbf{2}^{2+}$] and of triphenylene [(c) Cp, $\mathbf{5}^{2+}$; (d) Cp*, $\mathbf{4}^{2+}$] at −35 °C with 0.1 M n-$Bu_4N^+BF_4^-$ on Hg cathode. Same trend on Pt. Internal standard: ferrocene. The CV's of $\mathbf{3}^{2+}$ resemble those of $\mathbf{2}^{2+}$ (b). For values of E_p, ΔE_p, and i_a/i_c, see text and supplementary material. E_p's vary with scan rates only for the fourth wave of $\mathbf{4}^{2+}$ and $\mathbf{5}^{2+}$ (slow ET).

We find that the cyclic voltammogram (CV) of the precursor $Fe^{II}Fe^{II}$ dication $[(FeCp)_2(biphenyl)]^{2+}(PF_6^-)_2$, $\mathbf{1}^{2+}$,[3] shows, at −35 °C, only one two-electron wave (Figure 1a), i.e., the mixed valence $Fe^{I}Fe^{II}$ is not observable (at 20 °C, two waves were reported in the polarogram with ΔE = 100 mV[3a] which is now attributable to an EC mechanism). The reduction of $[Fe^{II}Cp(\eta^6\text{-arene})]^+PF_6^-$ by $LiAlH_4$ in THF −50 °C is known to result in ET:[4,5] $Fe^{II} \rightarrow Fe^{I}$. Applied to $\mathbf{1}^{2+}$, this reaction provides a deep blue, EPR-silent (4.2 K) solution of **1** (unstable above −30 °C) which, thus, cannot contain $Fe^{I}Fe^{II}$ or $Fe^{I}Fe^{I}$ species.[6] The working hypothesis is that a reversible structural and electronic rearrangement intervenes, concomitant to the second ET, and that the resulting energy gain lowers the potential of this second ET. Such a process is well documented in the 2e⁻ reduction of η^6-arene-Ru,[7] -Rh, -Ir,[8] and -Cr[9a] complexes to η^4-arene analogues,

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‡ Université du Maine (Mössbauer study).

§ Université de Rennes I (X-ray crystal structure).

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