measurements. Controlled-potential electrolysis at 1.3 V consumed 2 equiv of charge implicating the two-electron oxidation of **1** to a dinickel(III) species. The ligand itself and $[Zn_2L(H_2O)_2](ClO_4)_2$ do not show any electrochemical response in the entire potential range −2.0 to +1.7 V. The stability of the mixed-valence $Ni^{II}Ni^{I}$ and $Ni^{II}Ni^{III}$ species can be related to their conproportionation constants, K_{con}.[14,15] A greater value of K_{con} indicates greater stability of the mixed-valence species with respect to the isovalent species. Although $K_{con} = 3.8 \times 10^5$ for the reduction process implies considerable stability of the $Ni^{II}Ni^{I}$ species, a much lower value of K_{con} (2.3×10^2) for the oxidation process suggests easier access to the dinickel(III) species.

We note that there are many examples[1,16] of mononuclear macrocyclic Ni(II) complexes undergoing both oxidation and reduction. Also, there are limited number of examples[2,3] in which binuclear Ni(II) complexes undergo stepwise oxidation. However, to our knowledge, **1** provides the first example of a binuclear Ni(II) system exhibiting two successive one-electron oxidation steps as well as one-electron reduction steps.

Acknowledgment. We are very thankful to Dr. Debashis Ray for the X-ray structural work and to the Department of Science and Technology, New Delhi, for establishing a National Single Crystal Diffractometer Facility at the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science. Thanks are also due to Dr. S. K. Mandal for his assistance in the electrochemical measurements.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, H atom coordinates, NiN_2O_2 least-squares planes, and crystallographic details for **1** (8 pages); a listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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(15) K_{con} is defined in the following equation:

$$[Ni^{m+} - Ni^{m+}] + [Ni^{n+} - Ni^{n+}] \xrightleftharpoons{K_{con}} 2[Ni^{m+} - Ni^{n+}]$$

$K_{con} = \exp(nF(\Delta E)/RT)$, where $\Delta E = |E_{1/2}(1) - E_{1/2}(2)|$.

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A High-Valent Oxomanganese Dimer Containing Bridging and Terminal Inorganic Phosphate Ligands

The aqueous chemistry of high-valent manganese complexes has been the focus of our recent efforts both in terms of understanding the interactions of the water oxidation catalyst in photosystem II (PS II) with its substrate[1] and elucidating the primary process in the photoactivated assembly of this catalyst.[2] An important aspect of this work has been identifying ligands that are hydrophilic, oxidation resistant, and capable of stabilizing high-valence manganese centers. We report here the first bis(μ-oxo)manganese cluster with a bridging inorganic phosphate ion, a ligand that is attractive from all of the above standpoints. Additionally, the polyprotic character of ligated phosphate provides both a potential source and a sink for hydrogen ions in proton-coupled redox chemistry. Recently, we have demonstrated the presence of such proton-coupled electron transfer (PCET) for a bis(μ-oxo)dimanganese(III,IV) cluster.[3] In the water oxidation cycle of PS II, several of the individual light-induced oxidation events in the Mn cluster have been shown to be accompanied by hydrogen ion release,[4] which helps ameliorate the buildup of charge in the cluster; at present, there is no experimental evidence intimately coupling the electron transfer and proton release in these events in the PS II oxidation cycle. Since the coordination environment of the water oxidation catalyst in PS II is thought to involve primarily oxygen donor ligands,[5] incorporation of phosphate ligands into model clusters provides a route to a largely oxygen coordination environment about high-valent manganese. Our results indicate that inorganic phosphate promotes the stabilization of Mn(IV) in aqueous solution.

Wieghardt and co-workers[6] have reported the crystal structure of a μ_3-PO_4 trimeric manganese(IV) cluster, $[Mn_3(\mu\text{-}O)_3(tacn)_3(\mu_3\text{-}PO_4)]^{3+}$, which is the only other Mn cluster containing a bridging inorganic phosphate of which we are aware. The bridging phosphate bis(μ-oxo) dimer that we report here may provide a useful structural model for the dinuclear metal center in the purple acid phosphatase (PAP) enzyme. Current evidence suggests that phosphate can bind to the Fe(II,III/III,III) site in PAP as both a terminal and a bridging ligand.[7] Synthetic efforts have provided oxoiron complexes bridged by phenylphosphates,[8,9] and although a complex thought to contain bridging inorganic phosphates has been isolated, it has yet to be characterized crystallographically.[8] Such crystalline bridging phosphates may be elusive because of the hydrophilic nature of inorganic phosphate. PAPs have also been reported to contain Fe,Zn[10a] and Mn_2[10b] cofactors in place of the dinuclear iron center.

We have been investigating the aqueous chemistry of oxomanganese clusters such as $[(bpy)_2Mn(O)_2Mn(bpy)_2]^{3+}$ (**1**, bpy = 2,2′-bipyridine) in an effort to develop an understanding of the factors governing the coordination chemistry of high-valent Mn in H_2O in relation to photosynthetic water oxidation.[1,3] A number of simple Mn(III)–phosphate coordination compounds showing stability in aqueous solution are known.[12] We have previously reported that in acidic solution (pH 2, HNO_3), **1** undergoes disproportionation and cluster rearrangement to form the trinuclear complex $[Mn^{IV}_3(O)_4(bpy)_4(OH_2)_2]^{4+}$ (**2**), which consists of an $(Mn^{IV}(\mu\text{-}O)_2Mn^{IV})$ unit bridged by an O–Mn^{IV}–O linkage.[1] We now find that an unexpected version of this reaction occurs in H_3PO_4 solutions to give a species in which a $(Mn^{IV}(\mu\text{-}O)_2Mn^{IV})$ group is bridged by inorganic phosphate.

Treatment of an aqueous solution of **1** with H_3PO_4 (pH 2.3) generates a stable green solution, exhibiting a weak ($\epsilon \sim 100\ M^{-1}\ cm^{-1}$) absorption at 600 nm but now lacking the characteristic intervalence charge-transfer bands of **1** in the 700–900-nm region.[13] Slow crystallization from a 0.5 M H_3PO_4 aqueous solution yields[14] thin red-brown plate crystals of $[(bpy)(H_2PO_4)Mn(\mu$-

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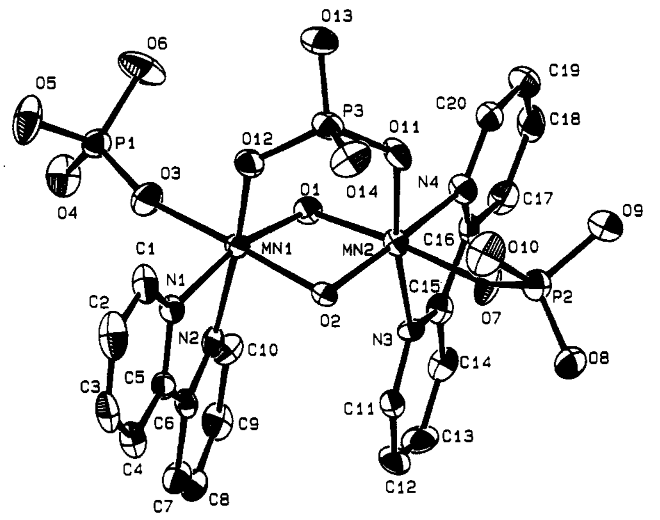


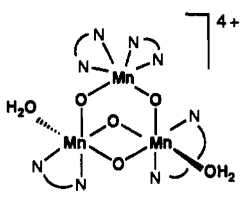
Figure 1. ORTEP of $[Mn_2(O)_2(\mu\text{-}HPO_4)(bpy)_2(H_2PO_4)_2]$ (3). Selected bond distances (Å) are given in Table II.

Table I. X-ray Experimental Details for Complexes 3 and 4

	3	4
empirical formula	$C_{20}H_{23}O_{15}N_4Mn_2P_3$	$C_{20}H_{27}O_{17}N_4Mn_2P_3$
fw	762.22	798.25
cryst dimens, mm	0.15 × 0.15 × 0.02	0.50 × 0.25 × 0.14
radiation	Mo Kα (λ = 0.71069 Å)	Cu Kα (λ = 1.54178 Å)
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P1$ (No. 2)
a, Å	15.533 (1)	10.552 (5)
b, Å	11.177 (1)	15.46 (1)
c, Å	15.961 (1)	9.682 (3)
α, deg		91.46 (4)
β, deg	105.895 (7)	106.26 (3)
γ, deg		106.06 (4)
V, Å^3	2665.1 (8)	1448 (1)
Z	4	2
ρ(calc), g/cm^3	1.900	1.830
μ, cm^{-1}	11.68	95.26
no. of reflcns measd	5456	3929
no. of reflcns included	2320 ($I \geq 3\sigma(I)$)	3056
cor	Lorentz–polarization, abs	
transm factors	0.92–1.05	0.85–1.51
params refined	397	423
R	0.045	0.055
R_w	0.048	0.070
max/min peak in final diff map, e/Å^3	0.43/–0.47	0.63/–1.03
goodness of fit	1.52	2.49

Table II. Comparison of Selected Interatomic Distances

	3	4
Mn–Mn	2.702 (2)	2.703 (2)
Mn1–O3	1.910 (5)	1.928 (5)
Mn2–O7	1.934 (5)	1.944 (5)
Mn1–O12	1.877 (5)	1.879 (4)
Mn2–O11	1.879 (5)	1.873 (5)
P3–O13	1.485 (6)	1.544 (5)
P3–O14	1.573 (5)	1.501 (5)
P3–O12 (Mn)	1.548 (6)	1.544 (5)
P3–O11 (Mn)	1.547 (6)	1.555 (5)
P1–O3 (Mn)	1.506 (5)	1.519 (5)
P1–O4	1.509 (6)	1.533 (5)
P1–O5	1.576 (6)	1.532 (5)
P1–O6	1.551 (6)	1.520 (6)
P2–O7 (Mn)	1.498 (5)	1.542 (5)
P2–O8	1.491 (6)	1.559 (8)
P2–O9	1.584 (6)	1.525 (8)
P2–O10	1.578 (6)	1.515 (7)
Mn1–N1	2.066 (6)	2.054 (6)
Mn1–N2	2.031 (6)	2.025 (5)
Mn2–N3	2.016 (6)	2.021 (6)
Mn2–N4	2.063 (6)	2.067 (7)



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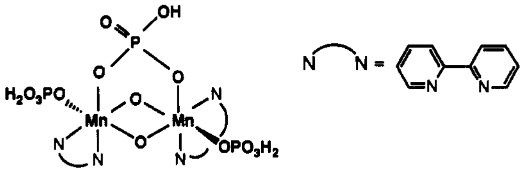

3

$HPO_4)(\mu\text{-}O)_2Mn(H_2PO_4)(bpy)]\cdot H_2O$ (3), in good yield. The equivalent weight of 3 was determined by iodometric redox titration to be 178 ± 15, in good agreement with a IV,IV dimer formulation for the metal centers. The structure as determined by X-ray diffraction is shown in Figure 1; crystallographic information is summarized in Table I. The complex contains two Mn(IV) centers bridged by two μ_2-oxo groups and one μ_2-phosphate; Mn–O and Mn–N bond lengths agree with those of other similar $Mn^{IV}{}_2(\mu\text{-}O)_2$ complexes cited in the literature.[15] It is noteworthy that the Mn–O bond lengths for the bridging and terminal phosphate pairs (Mn1–O3, Mn1–O12) and (Mn2–O7, Mn2–O11) differ by 0.033 and 0.055 Å, respectively, with the terminal bonds being longer. This finding indicates that it may be possible to distinguish between bridging and terminal phosphate in the PAP natural system by using Fe EXAFS.

Table II gives a summary of Mn–O(N) bond distances found for 3 and a structurally similar trihydrate (4), obtained in low yield by crystallization at 4 °C.[16] In 3, the location of protons on the phosphate oxygens (O5, O6, O9, O10, O14) is readily made by studying the relative P–O bond lengths; when protonated, the P–O distance is longer by 0.05–0.09 Å when compared to that of the other noncoordinated oxygens on the same phosphate moiety. Because the refinement of structure 4 is not as good as that for 3, the locations of the protons in 4 are not as clear. However, the noncoordinated P–O bond lengths on the bridging phosphate in 4 differ by only 0.033 Å as compared to a difference of 0.085 Å in 3. These data may indicate that 4 contains a fully deprotonated bridging phosphate and an H_3O^+ counterion. On the other hand, the terminal phosphates in 4 also do not show large differences in P–O bond lengths, even though a formal protonation state as seen in 3 is expected and should result in one shorter P–O bond. We also note that intermolecular hydrogen bonds are found to the oxygen atoms in the terminal phosphates in 4.

The mechanism of formation of 3 clearly involves a disproportionation pathway. Quantitative ^1H NMR spectroscopy shows that two bpy ligands are liberated for every molecule of cluster 1 dissolved in $D_2O\text{–}D_3PO_4$. A second product, containing high-

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(14) A solution of 2.70 g (2.38 mmol) of 1 in 25 mL of CH_3CN was filtered carefully and then added to 400 mL of 0.5 M H_3PO_4. The dark green solution, left undisturbed for 3 days at 22°C, yielded 225 mg of red-brown plates of 3 (12% yield). Anal. Calcd for $C_{20}H_{25}N_4O_{16}P_3Mn_2$: C, 30.79; H, 3.23; N, 7.18; P, 11.91; Mn, 14.08. Found: C, 30.59; H, 3.18; N, 7.11; P, 11.67; Mn, 13.97. Further solid can be collected; however, the purity of later crops is reduced by coprecipitation of another red, Mn-containing component of distinctly higher equivalent weight. Purification and characterization of this second complex is currently underway.

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(16) To 50 mL of water containing 0.5 mL of 85% H_3PO_4 was added 750 mg (0.66 mmol) of 1.[13] About 3 mL of this solution was placed in a test tube that was then stood inside a stoppered Erlenmeyer flask containing ~25 mL of concentrated H_2SO_4. After this flask was allowed to sit undisturbed at 4 °C for 3 weeks, ~10 mg of lustrous, dark red crystals of 4 were isolated, one of which was used for X-ray diffraction analysis.

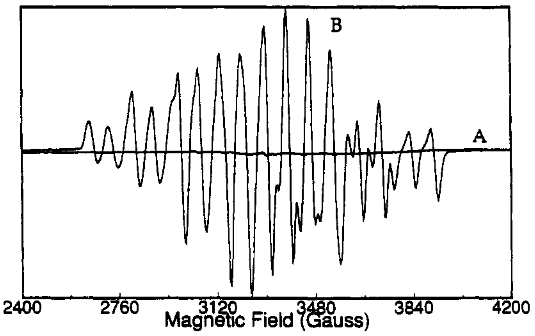

Figure 2. X-Band EPR spectrum at 9 K of (A) **1** (1 mM) in 0.1 M H_3PO_4 (pH 3) and of (B) solution A after addition of 0.05 M bpy (pH 4.5): microwave frequency, 9.05 GHz; modulation frequency, 100 kHz; modulation amplitude, 2 G; microwave power, 5 μW.

valent Mn, bpy, and PO_4 and having a considerably higher equivalent weight, has been isolated but is not yet fully characterized. These data can be summarized in eq 1 where the Mn(III)

$$2\,\mathbf{1} + H_3PO_4 \rightarrow [Mn^{IV}{}_2(\mu\text{-}O)_2(\mu_2\text{-}HPO_4)(bpy)_2(H_2PO_4)_2] + 4\,bpyH^+ + \text{“}[Mn^{III}{}_2(\mu\text{-}O)(\mu_2\text{-}H_2PO_4)_2(bpy)_2(H_2PO_4)_2]\text{”} \quad (1)$$

product cannot be fully defined. Proton-coupled disproportionation (eq 1) can be invoked for stabilizing the Mn(III) product; we have postulated[1] earlier that the disproportionation of **1** is made thermodynamically more favorable in acidic solution by protonation of a μ-oxo group in the (III,III) dimer. The presence of the strongly binding bridging phosphate must also play a significant part in stabilizing the (III,III) dimer since, in aqueous nitric acid at the same pH, the only low-valent product seen when **1** disproportionates to **2** is Mn^{2+}.

Further evidence for a disproportionation pathway is obtained by EPR spectroscopy. The green solutions prepared by the addition of **1** to an H_3PO_4 solution are EPR-silent (Figure 2A) having lost the characteristic 16-line spectrum of the III,IV dimer **1**. Adjusting the pH of this EPR-silent H_3PO_4 solution to 4.5 by the addition of 0.05 M pH 4.5 bpy buffer quantitatively regenerates **1** (Figure 2B), as determined by EPR and visible spectroscopy. Unlike the reaction of **1** in pH 2 HNO_3 where EPR demonstrates the presence of Mn^{2+} in addition to **2**, here the lack of any EPR signals for **1** dissolved in the H_3PO_4 medium rules out Mn^{2+} as the low-valent Mn species generated in the disproportionation reaction. Neither the (III,III) nor the (IV,IV) dimer would be expected to give an EPR spectrum.

The possible role of phosphate in stabilizing high-valent Mn clusters of biochemical interest is intriguing from a number of standpoints. First, the ubiquitous nature of phosphate makes it a possible ligand for high-valent Mn in biological systems. Second, it is clear that inorganic phosphate is a an excellent ligand for stabilizing Mn(IV). Acetate-bridged structures analogous to **3** have only been prepared in the (III,IV) but not the (IV,IV) oxidation state.[11,15,17] Christou has recently reported the formation of acetate-bridged Mn(III)–bpy dimers and tetramers in aqueous solution.[18] Thus, the additional stabilization provided by inorganic phosphate appears critical in achieving the (IV,IV) oxidation level. Finally, while the Mn_2 PAP remains incompletely characterized,[10] the interactions of inorganic phosphate with the metal centers may well be analogous to those for the Fe_2 PAP enzyme. With both terminal and bridging interactions being of potential importance in the PAP oxo cluster,[7] **3** provides an interesting system for comparison.

Acknowledgment. This research was supported by the Cooperative State Research Service, United States Department of Agriculture, through Agreement No. 90-37130-5575.

Supplementary Material Available: Complete ORTEP diagrams, text describing the solution of the structures, and tables of crystallographic data, atomic coordinates and isotropic thermal parameters, bond distances and angles, torsion angles, and anisotropic temperature factors for **3** and **4** (38 pages); tables of structure factors for **3** and **4** (37 pages). Ordering information is given on any current masthead page.

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Preparation of Phosphoraniminato Complexes Containing Polypyridyl Ligands. Nitrogen Atom Transfer from $[Os^{VI}(tpy)(Cl)_2(N)]^+$

A characteristic reaction of oxo complexes of the transition metals in high oxidation states is oxo transfer to such reductants as phosphines, sulfides, or olefins.[1-3] A parallel, nitrogen atom transfer chemistry has been established for complexes of Fe(V),[4] Mo(VI),[5] and Os(VI).[6] We recently described the preparation and crystal structure of the salt *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]Cl$ (**1**) (tpy is 2,2′:6′,2″-terpyridine). It was shown that this d^2 complex of Os(VI) could be reduced reversibly in aqueous solution to give the corresponding ammine complex of Os^{II}, $[Os^{II}(tpy)(Cl)_2(NH_3)]$, via the intermediate oxidation states, Os(V), Os(IV), and Os(III).[7] We report here that the redox chemistry of this complex extends to nitrogen atom transfer to PPh_3 and other phosphines. The product with PPh_3 is a paramagnetic phosphoraniminato complex of Os^{IV}. This complex, in turn, has an extensive redox chemistry of its own.

When *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]Cl$ (**1**) (λ_{max} = 525 nm)[7] was allowed to react with PPh_3 in acetonitrile, a rapid reaction occurred to give a new product with λ_{max} = 488 nm. On the basis of the results of a spectrophotometric titration with PPh_3 in acetonitrile, the stoichiometry of the reaction was shown to be 1:1. The reaction was first order in both PPh_3 and Os(VI) with $k(CH_3CN, 25\ °C) = 1.36\ (\pm 0.08) \times 10^4\ M^{-1}\ s^{-1}$ as shown by stopped-flow kinetics.

The product of the reaction was isolated and characterized as its hexafluorophosphate salt, *trans*-$[Os(tpy)(Cl)_2(NPPh_3)]PF_6$

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