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Mechanistic Studies on the Oxidation of Ascorbic Acid and Hydroquinone by a $\{Mn_4O_6\}^{4+}$ Core in Aqueous Media

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Supporting Information

ABSTRACT: Described in this work is the kinetics of oxidation of ascorbic acid and hydroquinone by a tetranuclear Mn(IV) oxidant, $[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+}$ ($\mathbf{1}^{4+}$, bipy =2,2′-bipyridine), in aqueous solution over a wide pH range 1.5−6.0. In particular, below pH 3.0, protonation on the oxo-bridge of $\mathbf{1}^{4+}$ results in the formation of $[Mn_4(\mu\text{-}O)_5(\mu\text{−}OH)(bipy)_6]^{5+}$ ($\mathbf{1H}^{5+}$) as an additional oxidant over $\mathbf{1}^{4+}$. Both ascorbic acid and ascorbate whereas only hydroquinone and none of its protolytic species were found to be reactive reducing agents in these reactions. Analysis of the rate data clearly established that the oxo-bridge protonated oxidant $\mathbf{1H}^{5+}$ is kinetically far more superior to $\mathbf{1}^{4+}$ in oxidizing ascorbic acid and hydroquinone. Rates of these reactions are substantially lowered in D_2O-enriched media in comparison to that in H_2O media. An initial one electron one proton transfer electroprotic rate step could be mechanistically conceived. DFT studies established that among the two sets of terminal and central Mn(IV) atoms in the tetranuclear oxidant, one of the two terminal Mn(IV) is reduced to Mn(III) at the rate step that we can intuitively predict considering the probable positive charge distribution on the Mn(IV) atoms.

$[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+} + R_{Red}$

↓ 1e, $1H^+$

$[Mn_4(\mu\text{-}O)_5(\mu\text{-}OH)(bipy)_6]^{4+} + R^+$

↓ fast

Products, Mn^{2+}, bipy, R_{Ox}

($R_{Red} = H_2A$ or H_2Q, R_{Ox} = A or Q, bipy = 2,2'-bipyridine)

INTRODUCTION

Manganese is known to be an essential metal for photosynthetic oxygen evolution, and it is now established that the oxygen-evolving complex (OEC) contains four manganese ions.[1−4] Bioinorganic model chemistry has played an extremely important role in the understanding of the OEC of photosystem II (PS II), the catalytic center of which contains Mn_4Ca cluster that accumulates four oxidizing equivalents before oxygen is formed, seemingly in the reaction: $2H_2O = O_2 + 4H^+ + 4e$. The OEC cycles through five redox states, $S_0 - S_4$, the index of which refers to the number of oxidizing equivalent stored.[5,6] Ligands derived from H_2O (O^{2-} or HO^-) are often present as bridges between the Mn atoms along with carboxylato moieties in the catalytic site.[7−9] Successive redox at Mn sites are definitely associated with a substantial change in the oxo-bridge (denoted by μ-O) basicity,[4a,7,8] and it is likely that a change in protonation state of the bridged metal cluster also occurs.[10]

Physical effects that generate on oxo-bridge protonation like changes in the magnetic behavior, increase in Mn···Mn distance and increase in redox potential are well studied.[11−15] However, chemical aspects resulting from oxo-bridge protonation have not been investigated much, and the investigations were primarily focused on acid−base behavior, mostly in non-aqueous media.[15,16] How such protonation affects the chemical reactivity of a synthetic model in aqueous media is not much explored, despite the relevance of such knowledge to PS II, which acts in water media.

The tetranuclear Mn^{IV}_4 complex investigated, $[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+}$ ($\mathbf{1}^{4+}$, bipy =2,2′-bipyridine, Figure 1) is easy to prepare,[13] water-soluble and stable in aqueous solution over a wide acidity range (pH, 1.5−6.0). On the basis of the oxidation state of its metal centers, $\mathbf{1}^{4+}$ formally corresponds to the fully oxidized, S_3 or S_4 state of OEC.[17,18] The one-electron reduced mixed-valent $Mn_3^{IV}Mn^{III}$ form of $\mathbf{1}^{4+}$ is one of the best EPR spectroscopic models for the S_2 state.[13] Mechanistic studies on the electron transfer reactions of $\mathbf{1}^{4+}$ thus appear to be potentially interesting.

Recently, we demonstrated that in some of its reactions[19] oxo-bridge protonated form of $\mathbf{1}^{4+}$, *viz.* $\mathbf{1H}^{5+}$, is kinetically superior oxidant to $\mathbf{1}^{4+}$. The present investigation was planned with two reducing species, ascorbic acid (H_2A) and hydroquinone (H_2Q) which have sufficient separation in their acidity values and in fact in our investigated acidity range, hydroquinone behaves as a neutral species, it does not dissociate to produce its conjugate base (*vide infra*). Thus, the proton-dependence on the observed rate, if any for hydroquinone redox should come only from the protolytic species of $\mathbf{1}^{4+}$ that could prove the involvement of

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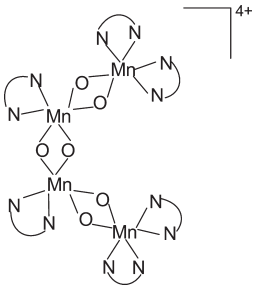

Figure 1. Schematic drawing of $[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+}$. N−N is 2, 2′-bipyridine.

oxo-bridge protonated species $\mathbf{1H}^{5+}$ in its redox. Interestingly, we found that both the reactions we report here are characterized by a basic mechanism of bioenergetic conversions, *viz*. proton coupled electron transfer and that might be a reason for reducing the activation barriers[20] for the apparently unfavorable oxidation of both ascorbic acid and hydroquinone by the title Mn_4 complex which itself is not a much powerful oxidant (*vide infra*). We further note in this context that both ascorbic acid and hydroquinone reduce Mn ions in PS II.[21] Furthermore, we are able to conclude from DFT studies that among the four Mn(IV) centers in $\mathbf{1}^{4+}$ or in $\mathbf{1H}^{5+}$, which particular one is reduced at the rate step.

EXPERIMENTAL SECTION

Materials. The complex salt hydrate $[Mn_4(\mu\text{-}O)_6(bipy)_6]$-$[ClO_4]_4 \cdot 2H_2O$ was synthesized following the literature procedure.[13] One of its water molecules is easily lost[13] and the elemental analyses of the material closely adhered to that expected for the monohydrate. The tetramer used here in all the experiments thus appears to be the sufficiently pure monohydrate. Anal. Calcd (in %) for $C_{60}H_{50}Cl_4Mn_4N_{12}O_{23}$: C, 43.16; H, 2.99; N, 10.07. Found: C, 43.39; H, 3.06; N, 10.00.

L-Ascorbic acid (G. R., E. Merck) was used as received. Stock solution of L-ascorbic acid of known concentrations was prepared by accurately weighing out the required amount and dissolving this quickly in deoxygenated water. Fresh solution were prepared prior to each experiment and diluted as per need. Care was taken to prevent oxidation and photo degradation of the L-ascorbic acid solution by storing it in dark when not in use. Hydroquinone (Aldrich, ≥ 99%) was recrystallized from ethanol and stored at 0 °C.[22] Preparation, standardization and storage of sodium nitrate (for maintaining the ionic strength) were described earlier.[23,24] 2,2′-bipyridine (Sigma) was used as received. D_2O (99.9 atoms %) was of Sigma or E. Merck grade. All other chemicals were of reagent grade and used as received. Doubly distilled, deionized, and then freshly boiled water was used throughout.

Equilibrium Measurements. The acid dissociation constants of ascorbic acid and hydroquinone were determined by pH metric titration with carbonate free NaOH solutions using a Metrohm (736 GP Titrino) autotitrator in both H_2O and in 95% D_2O media as described earlier.[22,23,25] A similar pH-metric titration of $\mathbf{1}^{4+}$ was performed in the pH range 2.0−6.0 to examine the basicity of its oxo-bridge.

Physical Measurement and Kinetics. The kinetics were monitored using a Hi Tech Scientific (Model LHX-150) Stopped-flow spectrophotometer at 420 nm where $\mathbf{1}^{4+}$ sufficiently absorbs using 1.00 cm quartz cells in the thermostatted (25.0 °C ± 0.2 °C) cell housing (water circulation, LKB-Bromma, Sweden). Most kinetic runs were performed at I = 1.0 M ($NaNO_3$) unless stated otherwise.

Stoichiometry and Reaction Products. The stoichiometry of the reactions was determined under both kinetic ([reducing agent] > [$\mathbf{1}^{4+}$]) and nonkinetic ([reducing agent] < [$\mathbf{1}^{4+}$]) conditions. A solution of the complex $\mathbf{1}^{4+}$ turned colorless (absorbance less than 0.01 at 380 − 800 nm) when an excess of either ascorbic acid or hydroquinone was mixed with it. The unused ascorbic acid was measured iodometrically using starch as indicator near the end point of the titration in a dilute H_2SO_4 media.[26] Iodine solution rapidly and quantitatively oxidizes ascorbic acid to dehydroascorbic acid[27] and a feasible estimation of unreacted ascorbic acid is thus possible. We noted that at the experimental condition I_2 formed an yellowish adduct with 2,2′-bipyridine but in no way that interfered with the determination as the yellowish adduct disappeared when ascorbic acid consumed I_2. The unused hydroquinone in the reaction mixture was quantified by titrating with ceric sulfate solution using diphenylamine indicator in dilute H_2SO_4 media to red-violet end point.[28] We observed that though ceric sulfate oxidizes 2,2′-bipyridine but the reaction is too slow to interfere with the stoichiometric experiments. Moreover, spectrophotometric titration of 0.10 mM of $\mathbf{1}^{4+}$ with varied amount of H_2A and H_2Q were carried out. The most likely oxidized product of hydroquinone is p-benzoquinone and that was proved by subjecting the product solution to thin layer chromatography (TLC) with a known standard solution of *p*-benzoquinone as described earlier.[22] Mn^{II} in the product solutions was estimated by EDTA titrations using EBT as indicator.[29] For this purpose, the Mn oxidant was reacted with excess reducing agents until the reaction mixture became colorless (absorbance less than 0.01 at 420 nm) and then the Mn^{II} was estimated. Any kind of interference from the product mixture was not found in this complexometric titration.

Computational Methods. All electronic structure calculations were carried out using Gaussian 09.[30] We have employed density functional theory (DFT) using M062X[31] which can properly deal with the dispersion energy and mixed basis set including the LACVP basis set to account for a nonrelativistic description of electron−core potentials (ECP's) for the Mn(IV) and Mn(III) centers, the basis 6-311+G(3df) sets for bridging O^{2-} ions were used to include polarization functions for μ-O species, and the 6-31G* basis sets for N-atoms and 6-31G were used for the rest of the atoms. The starting geometry of the Mn tetramer was taken from crystal structure of **LIDVUP** in Cambridge Structural Database by neglecting counteranion and water molecules. As the anions and water molecules are far away from the positive metal centers, the effect of these molecules on the coordination of the positive metal center would be minimal. The initial optimization was carried out with slightly loosen criteria of SCF convergence (10^{-4}) before the subsequent optimization with tight SCF option. CDIIS algorithm was used for all the SCF calculation whereby it turns on dynamic damping at early SCF iterations. The charge and spin multiplicity (denoted in parentheses) of the calculated complex species are as follows: $\mathbf{1}^{4+}$ (4,1), $\mathbf{1H}^{5+}$ (5,1), $\mathbf{1}^{3+}$ (3,2) and $\mathbf{1H}^{4+}$ (4,2). EPR spectra of $\mathbf{1}^{4+}$ at helium temperature showed the ground state of $\mathbf{1}^{4+}$ as the spin singlet. Although there have the possible presence of resonances from the higher spin states at the elevated temperatures,[13] the calculations in the present work are limited to the lowest spin state of each of the complex species. In the cases of $\mathbf{1}^{3+}$ and $\mathbf{1H}^{4+}$ the presence of spin contamination from the excited states of higher spin multiplicities were however noted.

Table 1. Stoichiometry of Reduction of the Mn^{IV}_4 (1^{4+}) Complex by Ascorbic Acid and Hydroquinone (T = 25.0 °C, C_{bipy} = [Hbipy$^+$] + [bipy] = 10.0 mM)

$[Mn^{IV}_4]$ (mM)	pH	$[H_2A]$ (initial) (=T_{H2A}) (mM)	$[H_2A]$ (left) (=T_{H2A}) (mM)	$[H_2Q]$ (initial) (=T_{H2Q}) (mM)	$[H_2Q]$ (left) (=T_{H2Q}) (mM)	$\Delta[Mn^{IV}_4]/\Delta[T_R]$
0.20	3.2	1.50	0.76			0.27
0.40	4.5	2.50	0.83			0.24
0.60	4.8	3.50	1.04			0.24
1.50	3.6	8.00	1.70			0.24
0.10	5.1	0.80	0.37			0.23
1.00	2.3	2.00				0.23[a]
						av = 0.24 ± 0.03
0.20	2.2			2.00	1.14	0.23
0.60	4.2			4.00	1.86	0.28
1.00	5.1			8.00	4.15	0.26
0.80	4.3			6.50	3.43	0.26
0.10	3.3			1.00	0.55	0.22
1.50	2.7			2.00		0.24[b]
						av = 0.25 ± 0.03

[a] [Mn(IV)] left after completion of reaction =0.54 mM. [b] [Mn(IV)] left after completion of reaction =1.02 mM.

All optimizations were followed by single point natural bond orbital (NBO) charge calculations.

RESULTS AND DISCUSSION

Stoichiometry and Reaction Products. Stoichiometric data (Table 1) clearly established a 1:4 stoichiometry (1^{4+}: reducing agent) for both the reactions whence it appears that the products of the reactions are dehydroascorbic acid (A) and *p*-benzoquinone (Q) respectively for the oxidation of ascorbic acid (H_2A, eq 1) and hydroquinone (H_2Q, eq 2). Moreover, TLC experiments clearly established p-benzoquinone as the sole product of hydroquinone oxidation.

$$[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+} + 4H_2A + 4H^+ \rightarrow 4Mn^{2+} + 6bipy + 4A + 6H_2O \quad (1)$$

$$[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+} + 4H_2Q + 4H^+ \rightarrow 4Mn^{2+} + 6bipy + 4Q + 6H_2O \quad (2)$$

Spectrophotometric titration also demonstrated a break-point at [1^{4+}]:[H_2A or H_2Q] = 1:4 (Figure 2) supporting the stoichiometry as described in eqs 1 and 2 where solution absorptions became practically zero, measured against a reagent blank comprising Mn^{2+} and bipy. The results of EDTA titrations of the product solutions revealed quantitative formation of Mn^{II} as the sole reduction product of Mn^{IV}.

Equilibrium Measurements. The average of at least 10 independent measurements in H_2O or in 95% D_2O media yielded the acid dissociation constants pK_{a1} = 4.00 (±0.1) for ascorbic acid and pK_{a1} = 9.85 (±0.15) for hydroquinone. These acidity values match quite well with the reported ones under similar conditions.[32,33] In 95% D_2O media, these values were found to be 4.28 and 9.95 for ascorbic acid and hydroquinone respectively that nicely agree with our earlier measurements.[22,25] All such values are at 25.0 °C and at I = 1.0 M ($NaNO_3$). The pH-metric titration of the title tetranuclear Mn oxidant, however, did not result in any ionization constant in the pH interval 1.5−6.0.

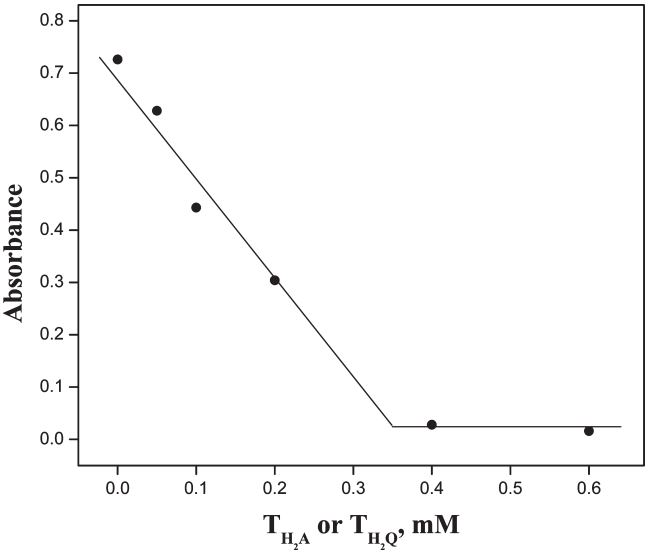

Figure 2. Spectrophotometric titration of 1^{4+} with ascorbic acid or hydroquinone. [1^{4+}] = 0.10 mM, pH = 5.01, [bipy] = 10.0 mM, I = 1.0 M ($NaNO_3$), T = 25.0 °C. Points shown in black solid circles are the experimental data and the solid lines represent linear least-squares fit.

Kinetics. No immediate spectral change was observed on mixing either reducing agent with 1^{4+} over the entire range of experimental pH and reducing agent concentrations. However, absorbance of 1^{4+} at 420 nm in presence of either of the reducing agent continuously decreased to less than 0.02 and plots of absorbance versus time could be well-fitted to standard first-order decay equation whence the first order observed rate constants (k_0) were evaluated in the usual way. A typical first-order decay for hydroquinone reaction is shown in Figure 3. Presence of excess bipy (pK_a of Hbipy$^+$ = 4.67 and that of H_2bipy^{2+} = 1.50)[34] controls any pH drift during the reactions well within 0.05 units. Presence or absence of dissolved oxygen did not alter the observed rate appreciably (mostly within 2−5%).

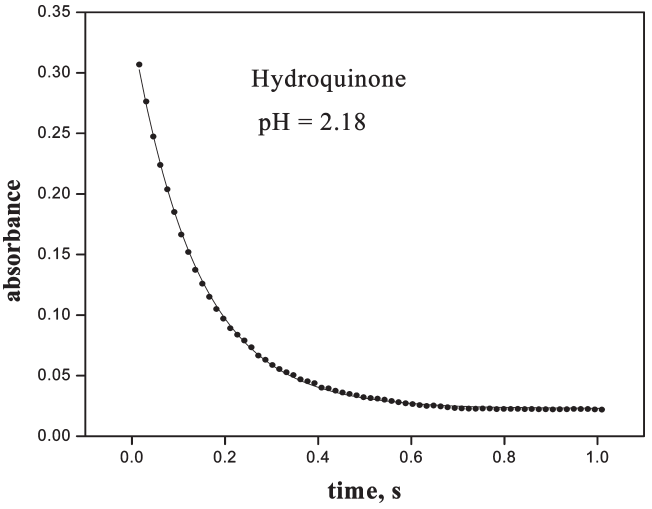

Figure 3. Representative absorbance versus time plot for the oxidation of hydroquinone by the tetranuclear Mn oxidant represents first-order decay of the tetranuclear Mn complex. $[\mathbf{1}^{4+}]$ = 0.05 mM, T_{H2Q} = 1.0 mM, I = 1.0 M ($NaNO_3$), [bipy] = 10.0 mM, T = 25.0 °C. The solid line is the best fit of the experimental data shown as solid circles.

Table 2. Some Representative First-Order Rate Constants for the Oxidation of Ascorbic Acid (H_2A) by the Tetranuclear Mn Oxidant at $[\mathbf{1}^{4+}]$ = 0.1 mM, T = 25.0 °C, [bipy] = 10.0 mM, I = 1.0 M ($NaNO_3$)

pH	T_{H2A} [M]	C_{bipy} [mM]	k_0 [s^{-1}]
1.53	0.001	10.0	60.0
1.90	0.001	10.0	38.3
2.22	0.001	10.0	24.0
2.81	0.001	10.0	18.0
3.00	0.001	10.0	16.9
3.50	0.001	10.0	20.9
4.18	0.001	10.0	31.0
4.50	0.001	10.0	35.0
5.00	0.001	10.0	40.0
5.50	0.001	10.0	42.1
6.00	0.001	10.0	43.0
3.02	0.002	10.0	35.8
3.01	0.003	10.0	47.8
3.02	0.005	10.0	80.0
2.80	0.001	5.0	18.7
2.79	0.001	20.0	19.4
2.83	0.001	40.0	18.3
2.81	0.001	60.0	18.3
4.17	0.001	10.0	44.0[a]
4.14	0.001	10.0	57.0[b]

[a] I = 0.5 M ($NaNO_3$); [b] I = 0.1 M ($NaNO_3$)

Average of k_0 values from at least three determinations was taken and the average coefficient of variation[35] for their measurements was well within 7%. The k_0 values remain unchanged when the reactions were carried out with varied complex concentration (0.025−0.20 mM), in presence of added 2,2′-bipyridine (1.0−60.0 mM) and at different monitoring wavelength in the region 380−530 nm.

Table 3. Some Representative First-Order Rate Constants for the Oxidation of Hydroquinone (H_2Q) by the Tetranuclear Mn Oxidant at $[\mathbf{1}^{4+}]$ = 0.1 mM, T = 25.0 °C, [bipy] = 10.0 mM, I = 1.0 M ($NaNO_3$)

pH	T_{H2Q} [M]	C_{bipy} [mM]	k_0 [s^{-1}]
1.51	0.001	10.0	25.3
1.82	0.001	10.0	15.0
2.18	0.001	10.0	6.77
2.35	0.001	10.0	4.93
2.53	0.001	10.0	3.75
2.80	0.001	10.0	2.65
3.33	0.001	10.0	1.60
3.85	0.001	10.0	1.55
4.20	0.001	10.0	1.52
4.31	0.001	10.0	1.49
5.02	0.001	10.0	1.62
6.00	0.001	10.0	1.50
2.81	0.002	10.0	5.62
2.82	0.004	10.0	10.18
2.80	0.006	10.0	16.65
2.52	0.001	20.0	3.56
2.53	0.001	40.0	3.60
2.52	0.001	60.0	3.71
5.04	0.001	10.0	1.66[a]
5.02	0.001	10.0	1.54[b]

[a] I = 0.5 M ($NaNO_3$); [b] I = 0.1 M ($NaNO_3$)

No influence of the added 2,2′-bipyridine (even at the 60 mM level) on the observed reaction rates refutes any importance of the bipyridine dissociation equilibrium (eq 3), presumably because the coordinatively saturated d^3 Mn^{IV} is inert to substitution.[36]

$$[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+} + H^+ + 2H_2O \rightarrow [Mn_4(\mu\text{-}O)_6(bipy)_5(H_2O_2)]^{4+} + [Hbipy]^+ \quad (3)$$

We further observed that both the reactions show good linear plots of k_0 versus T_R and there was no T_R independent term in either redox process (T_R = analytical concentration of the reducing agent, *viz.* $[H_2A] + [HA^-]$, or $[H_2Q]$). Some representative k_0 values are displayed in Tables 2 and 3.

Dependence of Rate on Acidity. The reactions were studied in the pH range 1.5−6.0. It was found that for both the redox, observed rate increases on increasing acidity of the reaction medium in the pH region *ca.* 1.5−3.0. We observed that during the entire pH range studied, the Mn^{IV}_4 tetramer is quite stable without appreciable decomposition (less than 10% decay in absorbance at 10 h at pH 1.5 and less than 10% decomposition after 24 h at pH higher than 2.8, measured at 420 nm). Thus the rate enhancement at lower pH is not due to any kind of acid-induced decomposition of the tetranuclear cluster. However, above pH 3.0 to pH 6.0, ascorbate oxidation rate was found to increase on increasing pH of the reaction medium whereas hydroquinone redox rate became unaltered within an allowable uncertainty (Tables 2 and 3). The same trend was found in D_2O media. The observed rate dependence on pH, as found in the low pH region, *viz.* pH 1.5 − 3.0 could only be explained if we assume a single protonation in $\mathbf{1}^{4+}$ resulting in the formation of $\mathbf{1H}^{5+}$ as protonated oxidants always react faster than their conjugate bases

Scheme 1

$$\mathbf{1}^{4+} + H^+ \overset{K_1}{\rightleftharpoons} \mathbf{1H}^{5+}$$

$$H_2A \overset{K_a}{\rightleftharpoons} H^+ + HA^-$$

$$\mathbf{1H}^{5+} + H_2A \xrightarrow{k_1} \text{Products}$$

$$\mathbf{1H}^{5+} + HA^- \xrightarrow{k_2} \text{Products}$$

$$\mathbf{1}^{4+} + H_2A \xrightarrow{k_3} \text{Products}$$

$$\mathbf{1}^{4+} + HA^- \xrightarrow{k_4} \text{Products}$$

Scheme 2

$$\mathbf{1}^{4+} + H^+ \overset{K_1}{\rightleftharpoons} \mathbf{1H}^{5+}$$

$$\mathbf{1H}^{5+} + H_2Q \xrightarrow{k_5} \text{Products}$$

$$\mathbf{1}^{4+} + H_2Q \xrightarrow{k_6} \text{Products}$$

within a system.[37] Both ascorbic acid (pK_{a1} = 4.00, this work; pK_{a2} = 11.3[33]) and hydroquinone (pK_a = 9.85; this work), being weak acids, do not practically dissociate in this low pH range and generation of any active reducing species like the conjugate bases of them may not be the case in point. On increasing pH from 3.0 to 6.0, progressive generation of ascorbate anion from ascorbic acid occurs with expectedly superior reactivity (as deprotonated reducing species are, in general, kinetically faster reducing agents[25,37c,38] and in fact in all known reactions ascorbate reacts faster than ascorbic acid in its redox)[25,39−41] and consequently rate increases, reaches a saturation at pH *ca.* 6.0 (Table 2) where ascorbate concentration becomes analytically equivalent to that of the total ascorbic acid used. The second dissociation of ascorbic acid (pK_{a2} = 11.3)[33] is too weak and could be neglected under the reaction condition employed here. Hydroquinone, on the other hand, being much lower acidic than ascorbic acid, do not dissociate up to pH 6.0 and thus rate becomes unaltered. Moreover, H_3Q^+ being a very strong acid (pK_a = −0.65)[42] may safely be assumed to be negligibly small to be reactive. Hydroquinone reaction with $\mathbf{1}^{4+}$ is thus a definite proof for the kinetically detected effect of oxo-bridge protonation of $\mathbf{1}^{4+}$at pH less than *ca.* 3.0.

We observed a linear variation of k_0 with T_R in the entire pH range studied and found no indication of rate saturation even at the highest T_R studied (Tables 2 and 3). A strong pre-equilibrium (K) binding of the reducing species with the Mn_4 oxidant ($\mathbf{1}^{4+}$) followed by the reaction of the intermediate thus formed with a second reducing species would lead to the observed linear dependence of k_0 on T_R provided that $KT_R \gg 1$.

The observed first-order rate constant for this scheme would be $k_0 = kT_R$ under the condition $KT_R \gg 1$, which requires a K value at least 10^4 (lowest T_R studied =2 × 10^{-3} M). However, the tetranuclear Mn oxidant is coordinatively saturated and inert to substitution at each Mn center and an inner-sphere attachment of reducing species seems unlikely. We thus disregard this kind of pathway in the kinetics of the redox process studied here. The observed proton dependence of k_0 could not be fitted to any type of reaction scheme without having an additional oxidant,

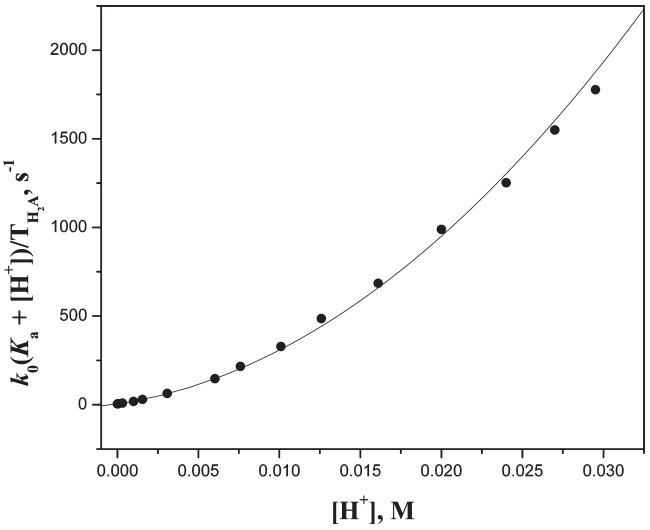

Figure 4. Plot of the left-hand-side of eq 4 versus $[H^+]$. $[\mathbf{1}^{4+}]$ = 0.1 mM, T = 25.0 °C, [bipy] = 10.0 mM, I = 1.0 M ($NaNO_3$). The values shown by solid circles are based on the observed first-order rate constants using the function $k_0(K_a + [H^+])/T_{H2A}$ as shown in the ordinate and the solid line represents eq 4.

$\mathbf{1H}^{5+}$, over $\mathbf{1}^{4+}$. Schemes 1 and 2, respectively, we suggest for the pathways of oxidations of ascorbic acid and hydroquinone.

We have also observed that the k_0 values were invariant on the ionic strength of the reaction media for hydroquinone redox (Table 3) whereas on decreasing ionic strength, rate increases for ascorbate redox (Table 2) suggesting reaction of neutral H_2Q and anionic species HA^- with cationic $\mathbf{1}^{4+}$ or $\mathbf{1H}^{5+}$.

The k_0 values in Table 2 could be best fitted by Scheme 1 for ascorbate redox and the k_0 values in Table 3 by Scheme 2 for hydroquinone redox. Scheme 1 and Scheme 2 lead to the rate laws presented by eqs 4 and 5, respectively, approximating $K_1[H^+] \ll 1$,

$$k_0(K_a + [H^+])/T_{H2A} = k_1K_1[H^+]^2 + (k_2K_1K_a + k_3)[H^+] + k_4K_a \quad (4)$$

where T_{H2A} is the analytical concentration of ascorbic acid defined by $[H_2A] + [HA^-]$ and $[H_2Q]$ is the analytical concentration of hydroquinone.

$$k_0/[H_2Q] = k_5K_1[H^+] + k_6 \quad (5)$$

The nonlinear least-squares values for k_1K_1, $(k_2K_1K_a + k_3)$ and k_4 as found by solving the second-order polynomial in $[H^+]$ (eq 4, Figure 4) and the linear least-squares values for k_5K_1 and k_6 (eq 5, Figure 5) are presented in Tables 4 and 5 respectively. These values reproduced the observed k_0 values acceptably well (deviation within 10%).

Tables 4 and 5 clearly demonstrate that $\mathbf{1H}^{5+}$ is kinetically far superior in oxidizing both H_2A or HA^- and H_2Q as $K_1 \ll 1$ and $(k_3)_{max} = 1.39 \times 10^4$ assuming the k_2 path does not contribute to the overall rate in the composite $(k_2K_1K_a + k_3)$. In fact, a very high reactivity of protonated oxo-bridged dinuclear Mn^{IV} species has been reported,[12,19] which are quickly reduced to lower states in presence of acids, indicating that the Mn^{IV} oxidation level is destabilized upon protonation of the oxo-bridge. Also, it is clear from Table 4 that $k_4 > (k_3)_{max}$ assuming k_2 path is absent and that firmly establishes HA^- reacts faster than H_2A. It is not possible to

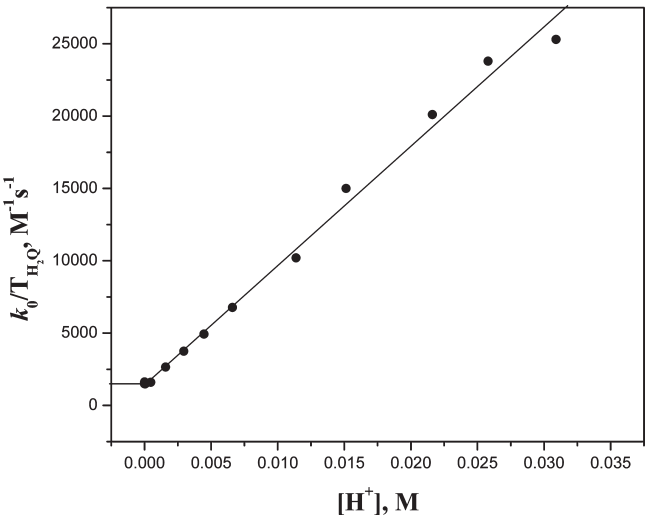

Figure 5. Plot of the left-hand-side of eq 5 versus $[H^+]$. $[\mathbf{1}^{4+}]$ = 0.1 mM, T = 25.0 °C, [bipy] = 10.0 mM, I = 1.0 M ($NaNO_3$).

Table 4. Second-Order Rate Constants for the Oxidation of Ascorbic Acid (H_2A) by the Tetranuclear Mn Oxidant at $[\mathbf{1}^{4+}]$ = 0.1 mM, T = 25.0 °C, [bipy] = 10.0 mM, I = 1.0 M ($NaNO_3$)

rate constants	ascorbic acid (H_2O) medium	ascorbic acid (95%D_2O) medium
k_1K_1 (M^{-2} s^{-1})	(1.70 ± 0.1) × 10^6	(6.77 ± 0.4) × 10^5
$(k_2K_1K_a + k_3)$ (M^{-1} s^{-1})	(1.34 ± 0.1) × 10^4	(5.66 ± 0.4) × 10^3
k_4 (M^{-1} s^{-1})	(4.20 ± 0.3) × 10^4	(1.30 ± 0.1) × 10^4

Table 5. Second-Order Rate Constants for the Oxidation of Hydroquinone (H_2Q) by the Tetranuclear Mn Oxidant at $[\mathbf{1}^{4+}]$ = 0.1 mM, T = 25.0 °C, [bipy] = 10.0 mM, I = 1.0 M ($NaNO_3$)

rate constants	hydroquinone (H_2O) medium	hydroquinone (95% D_2O) medium
k_5K_1 (M^{-2} s^{-1})	(8.31 ± 0.5) × 10^5	(2.78 ± 0.2) × 10^5
k_6 (M^{-1} s^{-1})	(1.50 ± 0.1) × 10^3	(620 ± 40)

conclusively compare the reactivities of H_2A or HA^- in reducing $\mathbf{1H}^{5+}$ or $\mathbf{1}^{4+}$ as k_2 and k_3 paths are proton-ambiguous, but with a common view that deprotonated reductants react faster than their neutral conjugate acids[25,37a,39−43] and ascorbate (HA^-) reacts much faster than ascorbic acid (H_2A) in its known redox reactions,[25,39−41] a significant contribution of k_2 path is anticipated particularly when k_4 path significantly contributes. The unmistakable dominance of the k_1 or k_5 paths may be attributed to hydrogen-bonding involving the protonated oxo-bridge and the reducing species that renders a closer proximity of the redox species, in addition to the higher positive charge of the protonated species $\mathbf{1H}^{5+}$ compared to $\mathbf{1}^{4+}$.

In deriving the rate eqs 4 and 5, we approximated $K_1[H^+] \ll 1$ so that $T_{Mn} \approx [\mathbf{1}^{4+}]$. This inequality along with the k_1K_1 or k_5K_1 values listed in Tables 4 and 5 estimate a range for K_1 between 10^{-5} and 1. The fact that $K_1[H^+]$ is much less than 1 sets an upper limit for the pre-equilibrium binding K_1 nearly at 1 as the maximum $[H^+]$ used in this study is *ca.* 10^{-1} (M), while assuming the diffusion-controlled limit is 10^{11} $M^{-1}s^{-1}$ the lower limit of K_1 estimated from the k_1K_1 or k_5K_1 values in Tables 4 and 5 is *ca.* 10^{-5}. Though we are unable to more precise estimate of K_1, a low value is anticipated as we got no spectral changes (UV/vis) of the Mn_4 complex in the entire pH range 1.5−6.0. Reports so far available for the very low basicities of oxo-bridges linked to the high-valent Mn^{IV} centers[16d,44] support the approximations $K_1[H^+]$ and K_1 both are much less than 1. The strong acidity of the protonated oxo-bridge may thus be inferred.

Mechanism. We observed that the decay of $Mn^{IV}{}_4$ follows a purely first-order kinetics that is a single exponential decay of $Mn^{IV}{}_4$ concentration (Figure 3) and an initial one-electron transfer rate-limiting step in the overall eight electron transactions (eqs 1 and 2) is proposed that results in the intermediate mixed-valence species $Mn^{IV}{}_3Mn^{III}$, which is likely to be reduced quickly in the following steps by the excess reducing agents or the radicals generated there from at the rate step. The follow-up reactions must be rapid due to the reasons that: the reducing agents may be highly reactive radical species in addition to the pure reducing agents and that the most likely one electron reduced species of $\mathbf{1}^{4+}$ or $\mathbf{1H}^{5+}$, *viz.* $[Mn^{IV}{}_3Mn^{III}(\mu\text{-}O)_6(bipy)_6]^{3+}$ is very unstable, even at low temperature (190 K)[45]— the very high reactivity of this species, produced from the cryogenic radiolytic reduction of $\mathbf{1}^{4+}$ has been documented.[45] Moreover, during the reduction of $\mathbf{1}^{4+}$ to Mn^{II}, tri or dinuclear species that might generate could bear two to four H_2O molecules bound to Mn centers. Such aqua complexes are known to be very reactive in redox processes.[46]

The electrochemical aspects of the title tetramer was studied in detail by Dunand-Sauthier[47] and Girerd.[13] The cyclic voltammogram of $\mathbf{1}^{4+}$ in bipy/$Hbipy^+$ buffer shows only one irreversible reduction peak near at 0.40 V (vs. Ag/AgCl)[47] that leads to the formation of $[Mn(bipy)_3]^{2+}$ species. Attempts at single-electron electrochemical reduction of $\mathbf{1}^{4+}$ just before the first one-electron reduction wave resulted in the formation of Mn^{II}. Color fading of the solution and EPR spectroscopic evidence clearly established decomposition of the tetranuclear complex into four Mn^{II} ions.[13] Standard chemical reduction in solution also failed to achieve the monoreduced form.[13] Exhaustive reduction of $\mathbf{1}^{4+}$ at 0.20 V (vs. Ag/AgCl) consumes almost eight equivalents of electrons per mole of $\mathbf{1}^{4+}$ and leads to Mn^{II} *via* the intermediate generation of the mixed-valent dinuclear species $[Mn^{IV}Mn^{III}(\mu\text{-}O)_2(bipy)_4]^{3+}$.[47a] This mixed-valent species, however, could not be generated selectively and quantitatively as reduction of the $Mn^{IV}{}_4$ and $Mn^{IV}Mn^{III}$ mixed valent species occurs at a very similar potential (0.40 V vs. Ag/AgCl).[47] We also did not observe formation of any such spectrally characterizable dinuclear intermediate during the chemical reduction of the title oxidant with ascorbic acid or hydroquinone when the latter are used in concentrations stoichiometrically deficit to that of $[\mathbf{1}^{4+}]$. All such facts clearly establish the very high reactivity of $[Mn^{IV}{}_3Mn^{III}(\mu\text{-}O)_6(bipy)_6]^{3+}$ which is the one-electron reduced species of $\mathbf{1}^{4+}$. The tetranuclear $[Mn^{IV}{}_4(\mu\text{-}O)_6(bipy)_4]^{4+}$ ($\mathbf{1}^{4+}$) cluster is much less oxidizing than the dinuclear $[Mn^{IV}{}_2(\mu\text{-}O)_2(bipy)_4]^{4+}$ cluster.[13,48] An analogous observation has been reported[49] for the trinuclear species $[Mn^{IV}{}_3(\mu\text{-}O)_4(bipy)_4]^{4+}$. The terminal sites $(bipy)_2Mn^{IV}(\mu\text{-}O)_2$ at a first sight is expected to be as oxidizing as the identical sites in the dinuclear $[Mn^{IV}{}_2(\mu\text{-}O)_2(bipy)_4]^{4+}$ units. However, the 4+ charge is shared by more atoms in the tetranuclear ($\mathbf{1}^{4+}$) species and that explains the lesser oxidizing capability of the terminal sites $(bipy)_2Mn^{IV}(\mu\text{-}O)_2$ in $\mathbf{1}^{4+}$.[13] Nevertheless, $\mathbf{1}^{4+}$ more rapidly oxidizes both

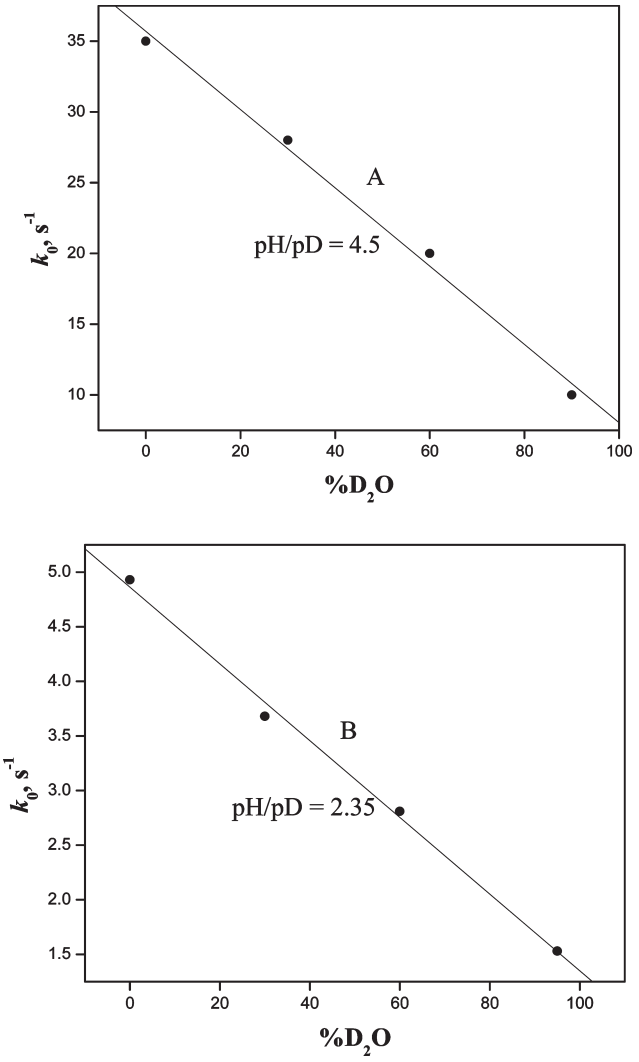

Figure 6. Effect of the amount of D_2O (mol %) on k_0. [$\mathbf{1}^{4+}$] = 0.1 mM, T = 25.0 °C, [bipy] = 10.0 mM, I = 1.0 M ($NaNO_3$), A: H_2A, [H_2A] = 1.0 mM, B: H_2Q, [H_2Q] = 1.0 mM. pH/pD conversion was done using the relation: pD = $pH_{measured}$ + 0.40; see, for example ref 63.

ascorbic acid and hydroquinone than the Mn^{IV}_2 dimer[50] although both 1e and 2e oxidations of the two reducing agents are quite endothermic.[51]

Although the exact one-electron potential of $\mathbf{1}^{4+}$ could not be measured, one may test whether an outer-sphere mechanism for electron transfer is operative or not at least for ascorbate oxidation using a simplified Marcus cross-relation $k_{12} = (k_{11}k_{22}K_{12})^{1/2}$ by comparing the reactivity ratio of ascorbate (HA^-) to ascorbic acid (H_2A). It could be checked that for any value of E^0_{Red} ($\mathbf{1}^{4+}/\mathbf{1}^{3+}$), the $(k_{12})_{HA^-}/(k_{12})_{H2A}$ should be 7.9 × 10^7. For these calculations we have used literature values of the self-exchange rate constants for H_2A and HA^- as well as their redox potentials.[52] Table 4, however, clearly shows only a little more reactivity of HA^- over H_2A in reducing $\mathbf{1}^{4+}$ or $\mathbf{1H}^{5+}$ as $k_4/(k_3)_{max}$ or $(k_2)_{max}/k_1$ both are at best at the level of 10^2. Such a situation clearly disfavors a pure outer-sphere electron transfer.

In order to further explore the electron-transfer mechanism we measured several k_0 values in D_2O enriched media and the second-order rate constants or their composites are displayed in Tables 4 and 5 that clearly establishes kinetic isotope effects. The

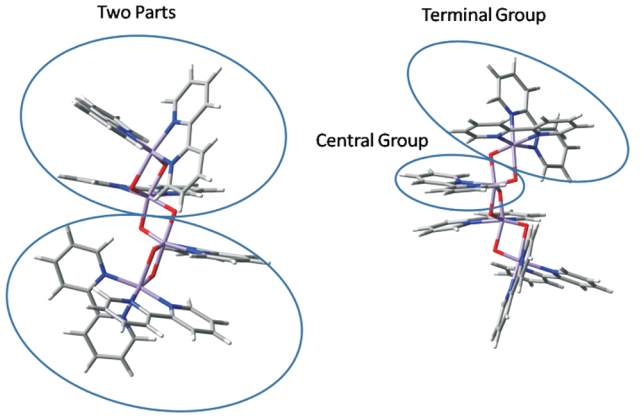

Figure 7. The $\mathbf{1}^{4+}$ species could be looked as a combination of two equivalent parts. Each part is a combination of terminal and central groups.

lowering of rate in D_2O media indicates the occurrence of electroprotic mechanism[53] in both the reactions. Moreover, we also found that the rate decrease in H_2O/D_2O mixed-media are linearly related to the D_2O content of the mixed solvent (Figure 6) suggesting transfer of a single proton at the rate step of both the reactions.[54]

As discussed, an initial one-electron transfer rate step results in the formation of highly reactive mixed-valent Mn species $Mn^{IV}_3Mn^{III}$ that is likely to be reduced very quickly in the solution by the excess reducing agents or the radicals generated at the rate steps of the two reactions.

We did not, however, observe any polymerization in either redox when the reactions were carried out in 6% v/v acrylonitrile, although this does not necessarily mean the production of radicals as they may react faster with one-electron reduced Mn species, which is itself highly reactive. The one-electron reduced species of $\mathbf{1}^{4+}$ or $\mathbf{1H}^{5+}$ must have much more basic oxo-bridges than the oxo-bridges in $\mathbf{1}^{4+}$ or $\mathbf{1H}^{5+}$ (due to reduction of one positive charge in $\mathbf{1}^{4+}$ or in $\mathbf{1H}^{5+}$ in forming their one-electron reduced species) that immediately accept a proton from reaction medium, which removes thermodynamic or kinetic barriers to further reduction.[55] Results of our DFT studies (*vide infra*) also corroborated that upon one-electron reduction, the negative charge on the oxo-bridges of both $\mathbf{1}^{3+}$ and of $\mathbf{1H}^{4+}$ have increased. A remarkably large increase in the basicity of oxo-bridges in the 1e reduced mixed-valent species in di or polynuclear Mn complexes is well-documented[55b,56] and is a key feature in the sequential redox steps of the Kok cycle in PS II.[18,57] An analogous situation of the increased in basicity of oxo-bridges of the reduced metal centers is also proposed in the chemical reduction of μ-oxo diiron(III) compounds.[20c,25,55b,56,58]

We have observed a substantial decrease in the rate constants in D_2O enriched media compared to those in H_2O media. However, since long back it is known that D_2O has a smaller autoprotolysis constant than H_2O by a factor of 5[59] and thus it is less basic than D_2O which means that the oxo-bridges in the title oxidant will be able to compete with the solvent for the D^+ in D_2O more effectively than for the H^+ in H_2O. An increase K_1 value (Scheme 1 or 2) is thus expected in D_2O media. In general, weak acids in H_2O become weaker in D_2O.[59,60] Literature shows some precedence where rate increases significantly with D_2O content in an H_2O/D_2O mixture if acid−base pre-equilibrium steps are involved prior to the rate steps.[59,60a,60b] So, the true rate

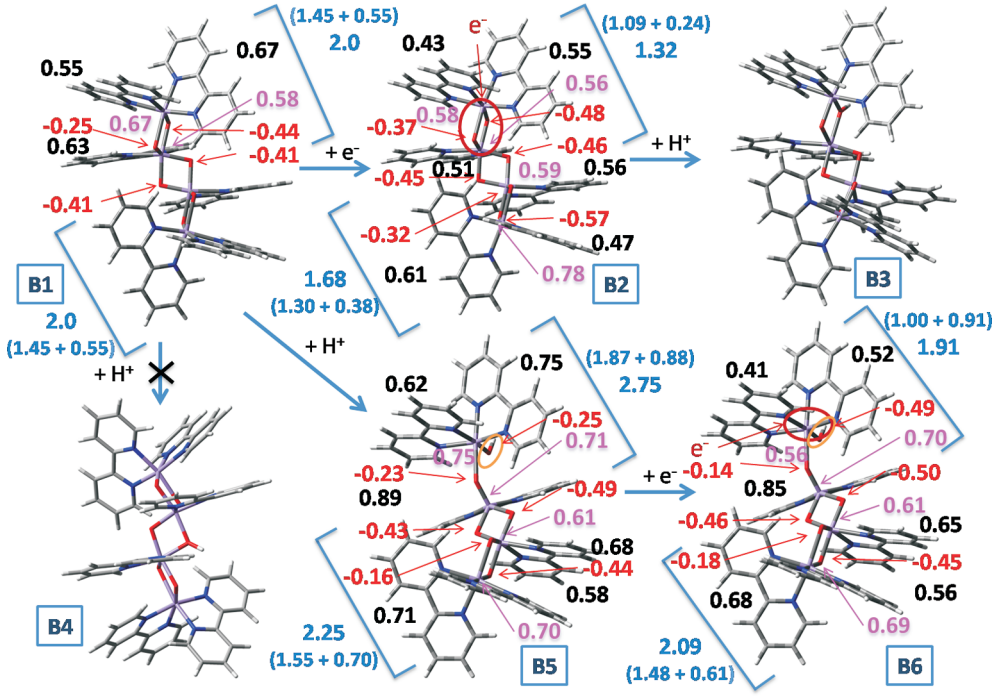

Figure 8. NBO Charges of the parent $\mathbf{1}^{4+}$ species and species generated from $\mathbf{1}^{4+}$. Magenta color: Mn centers, Red color: Oxygen centers. Black color: Sum of charges of atoms in terminal and central independent bipyridines. Blue color: Sum of atomic charges of the two opposite groups of the complex consisting of terminal groups (first value in parentheses) and central groups (second value in parentheses).

constants k_1 and k_2 (not their composites as shown in Table 4) are much more lowered in their magnitudes in D_2O media (though it should be kept in mind that the K_{a1} value of ascorbic acid is also lowered in D_2O media).

Among the four six-coordinate Mn^{IV} centers in the title complex, the two terminal Mn atoms are equivalent in the sense that each is ligated to two bipy ligands along with two oxo ligands whereas each of the two equivalent middle (central) Mn atoms are ligated to four oxo atoms and one bipy ligand (Figure 1). The positive charge density on either of these two kinds of Mn atoms is not expected to be similar. The two terminal Mn atoms that bind with two oxo ligands and two bipy ligands should bear more positive charge than the two central ones due to the binding of four strongly electron donating oxo ligands in each. Moreover, each of the two terminal Mn centers has two π-accepting bipy ligands whereas the two central Mn atoms carry only one bipy ligand. The one-electron rate steps (k_1 to k_6) shown in Schemes 1 and 2 should thus involve either of the two terminal Mn atoms.

Theoretical Studies. Reduction of the title teranuclear Mn oxidant as described in earlier section proceeds through parallel paths involving $\mathbf{1}^{4+}$ and $\mathbf{1H}^{5+}$, and mechanistically as described earlier, we propose a one-electron rate step generating $Mn^{IV}{}_3Mn^{III}$ species and we have had chemical reasons to believe that one of the two terminal Mn(IV) atoms is reduced at the rate step. We performed theoretical calculations to check our chemical intuitions that one of the terminal Mn(IV) atoms is reduced at the rate step.

To begin the theoretical studies, the whole $\mathbf{1}^{4+}$ species could be looked as a combination of two equivalent parts. Each part is a combination of terminal and central groups as described in Figure 7 below. The terminal groups contain terminal Mn(IV) centers coordinated with 4 N atoms (2 bipy rings) and one oxygen atom while 2 N atoms (1 bipy ring) and two oxygen atoms for the central groups. Moreover, note that the selection of oxygen atoms for the terminal and central groups is based on a distance factor—respective oxygen atoms nearer to the terminal/central Mn atoms are included in defining the terminal or central groups (Table S1 and Figure S1, Supporting Information show Mn−O and Mn−N covalent bond lengths along with atom labeled pictorial diagram of $\mathbf{1}^{4+}$).

Figure 8 shows charge distribution on the parent $\mathbf{1}^{4+}$ species (Figure $8B_1$) and on species generated on adding one electron to $\mathbf{1}^{4+}$ (Figure $8B_2$) or one proton to $\mathbf{1}^{4+}$ generating $\mathbf{1H}^{5+}$ (Figure $8B_5$) and its subsequent one-electron reduced product (Figure $8B_6$). To resolve which Mn atom (terminal or central) in $\mathbf{1}^{4+}$ is reduced to produce $Mn^{IV}{}_3Mn^{III}$, a comparison of charge distribution in $\mathbf{1}^{4+}$ and in $\mathbf{1}^{3+}$ (Figure $8B_1$ and Figure $8B_2$ respectively), would be helpful. Figure $8B_1$ and Figure $8B_2$ clearly show that the positive charge reduction is slightly larger for the terminal group (0.36) in comparison to that for the central group (0.31) indicating reduction of terminal Mn(IV). In terms of the charges of the Mn centers, the charge of one of the terminal Mn(IV) center changes from 0.67 in $\mathbf{1}^{4+}$ to 0.58 in $\mathbf{1}^{3+}$ whereas for the central Mn(IV) the change is only marginal (0.58 to 0.56). Moreover, considering the LUMO, it is clear that the vacant antibonding orbitals are located mainly on the central/terminal Mn and O-atoms. Also, considering the HOMO of the one-electron reduced species $Mn^{IV}{}_3Mn^{III}$, *viz.* $\mathbf{1}^{3+}$, it is seen that the added electron density is relatively more distributed on terminal Mn atom in comparison to the central one, furthermore the electron density is also distributed in large extent at the bridging oxygen atoms of both the terminal and central groups and in lesser extent at the bipy rings. Overall, one may argue that there might be a possibility of μ-O and bipy mediated reduction of terminal Mn(IV) atom. Subsequent protonation on an oxo-bridge of $\mathbf{1}^{3+}$ leads to $\mathbf{1H}^{4+}$. Among the oxygen atoms in $\mathbf{1}^{3+}$, the oxygen with highest negative charge (−0.48) which is the

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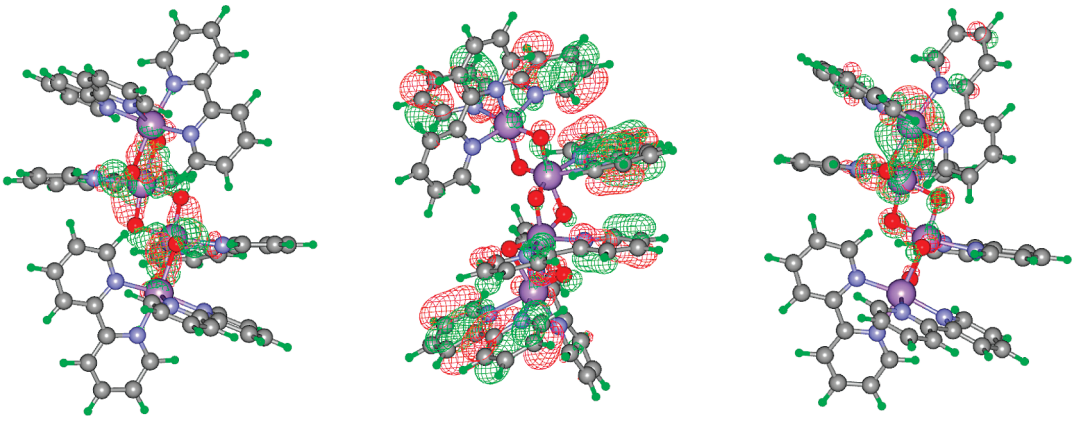

Figure 9. (Left to right) LUMO, HOMO orbitals of $\mathbf{1}^{4+}$ and HOMO orbital of $\mathbf{1}^{3+}$.

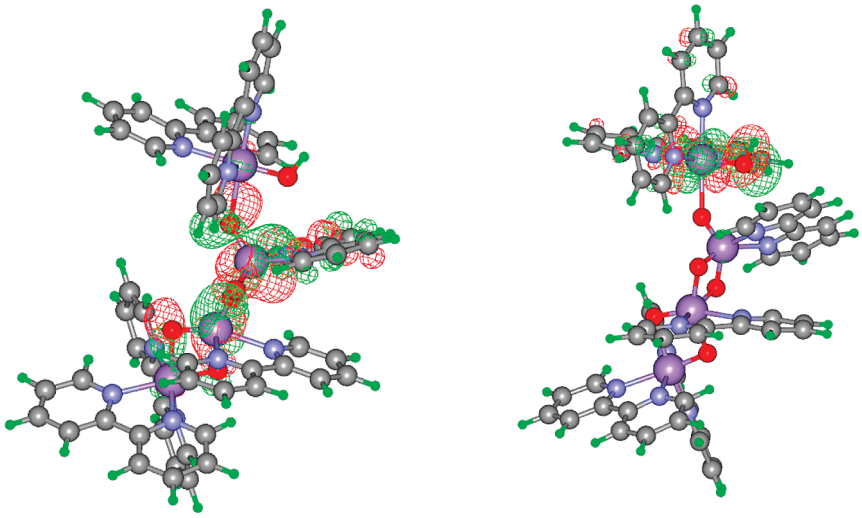

Figure 10. LUMO and HOMO orbitals of $\mathbf{1H}^{5+}$ and $\mathbf{1H}^{4+}$.

terminal oxygen as shown in Figure $8B_2$ will be protonated producing $\mathbf{1H}^{4+}$ (Figure B_3). In particular, HOMO of $\mathbf{1}^{3+}$ (Figure 9) clearly explains the availability of molecular orbital in the terminal oxygen which could be easily accessible for protonation.

In a parallel path, as described in the Kinetics section, $\mathbf{1H}^{5+}$ (formed by protonation of $\mathbf{1}^{4+}$) reacts. Among the oxygen atoms of the oxo-bridges in $\mathbf{1}^{4+}$, that oxygen which carries highest negative charge will be protonated to form $\mathbf{1H}^{5+}$. Considering the terminal and central oxygen atoms, we find that the terminal oxygen atom has −0.44 charge whereas one of the central oxygen has somewhat reduced charge (−0.25) due to the aromatic CH···O interactions (∼ 2.4 Å) involving central and terminal bipy rings of $\mathbf{1}^{4+}$ (Figure S2, Supporting Information). Two central oxygen atoms have equal charges (−0.41). It is thus expected that the terminal oxygen atom with −0.44 charge is protonated whereas central oxygen atoms (−0.41 charge on each) will not be protonated (Figure $8B_4$). Figure $8B_5$ shows the protonated OH-group in $\mathbf{1H}^{5+}$ with relatively decreased total charge of −0.25 due to protonation. HOMO of $\mathbf{1}^{4+}$ (Figure 9) clearly shows that one of the terminal oxygen has the availability of molecular orbital which could be the protonation site. In addition, we note that the covalent bond between Mn and oxygen atom of OH group is broken (Figure 8, parts B_5 and B_6) that generates 'somewhat opened' Mn(IV) (unsaturated metal center) with increased reactivity, hence the protonation step could be the initial step toward the reductive decomposition of the $\mathbf{1}^{4+}$ complex in multiple steps. The protonation after one electron reduction of the terminal Mn(IV) in $\mathbf{1}^{4+}$ (Figure 8, parts B_2 and B_3), however, does not give rise to the breakage of the Mn−OH coordination bond.

Next is the one-electron reduction issue of $\mathbf{1H}^{5+}$. Here also terminal Mn(IV) is reduced as expected from charge calculations. The charge reduction in the terminal group (already protonated center) for the conversion $\mathbf{1H}^{5+}$ to $\mathbf{1H}^{4+}$ (Figure $8B_5$ to Figure $8B_6$) is much more (1.87 to 1.00) than in the central group (0.88 to 0.91) which is associated with the terminal Mn(IV) charge reduction from 0.75 to 0.56 whereas only a marginal charge reduction of central Mn(IV) is seen (0.71 to 0.70). Considering LUMO (Figure 10) of $\mathbf{1H}^{5+}$, the antibonding orbitals are located at the central Mn centers and also partly distributed at the N-atoms of central bipy and oxo-bridges. In contrast, the HOMO of $\mathbf{1H}^{4+}$ (Figure 10) clearly shows excess electron density is located on the terminal Mn center along with OH-group and terminal bipy groups. Therefore, here also like that for $\mathbf{1}^{4+}$, reduction is most likely involved the terminal Mn(IV) associated with OH and terminal bipy groups.

The electrochemical reduction of Ru^{II}−bipy complexes ends at the product spectrum where the excess electron resides at the bipy rings (no metal reduction) that clearly demonstrates the electron-acceptance properties of bipy rings. The electron spin resonance data for the reduced one, two, and even three electron species were found to be consistent with $[Ru(bipy)_2(bipy^-)]^+$, $[Ru(bipy)(bipy^-)_2]$, and $[Ru(bipy^-)_3]^-$ species.[61] In the present Mn^{IV} system with obvious higher electron affinity due to the 4+ state of Mn atoms, we find the ultimate reaction product is Mn^{II}, but the electron transfer as discussed might be mediated by bipy rings.

As discussed in the earlier sections, we propose a one-electron transfer rate step producing mixed-valent $Mn_3^{IV}Mn^{III}$ species that quickly decomposes to products in presence of heavy excess reducing agent. Increased basicity of the oxo-bridges in the one-electron reduced mixed-valent species favors a simultaneous proton transfer to the oxo-bridge (schematically shown in B_2 to B_3 conversion in Figure 8). In another parallel path $\mathbf{1H^{5+}}$ oxidizes the reducing agents. In species shown in Figures $8B_3$ and in $8B_5$ we propose protonated oxo-bridges. In some known Mn^{IV} complexes with oxo and hydroxo-bridges, crystallographic data shows that Mn−OH distances are substantially longer than Mn−O distances[11] that might indicate more reactivity of Mn center connected to protonated oxo-bridge (Mn−OH) and in fact, higher reactivity of $\mathbf{1H^{5+}}$ than $\mathbf{1^{4+}}$ in oxidizing ascorbate and hydroquinone has been found (Tables 4 and 5) in this investigation. The optimized geometries of $\mathbf{1H^{5+}}$ and $\mathbf{1H^{4+}}$ show no coordination bond between the central Mn atom and the protonated oxygen clearly indicating a somewhat "opened" Mn center for increased reactivity—a cluster break up is anticipated. Increased reactivity that includes cluster break-up,[62,48] inhibition of catalase activity[14] and commencement of disproportionation[16a] on oxo-bridge protonation are experimentally well-documented in multinuclear Mn complexes.[11−16]

■ ASSOCIATED CONTENT

Supporting Information. Mn−O and Mn−N covalent bond lengths in $\mathbf{1^{4+}}$, atom labeled pictorial diagram of $\mathbf{1^{4+}}$ and aromatic CH···O interaction in $\mathbf{1^{4+}}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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