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Valence Tautomerism in a High-Valent Manganese–Oxo Porphyrinoid Complex Induced by a Lewis Acid

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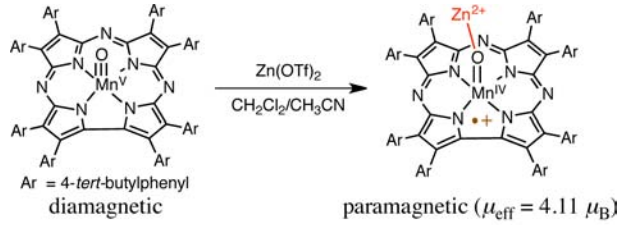
Supporting Information

ABSTRACT: Addition of the Lewis acid Zn^{2+} to $(TBP_8Cz)Mn^{V}(O)$ induces valence tautomerization, resulting in the formation of $[(TBP_8Cz^{+\bullet})Mn^{IV}(O)–Zn^{2+}]$. This new species was characterized by UV–vis, EPR, the Evans method, and ^1H NMR and supported by DFT calculations. Removal of Zn^{2+} quantitatively restores the starting material. Electron-transfer and hydrogen-atom-transfer reactions are strongly influenced by the presence of Zn^{2+}.

Redox-inactive metal ions serving as Lewis acids have recently come under scrutiny for their potential influence on the reactivity of biologically relevant transition metal centers. The influence of redox-inactive metal ions on high-valent Mn–oxo species is of particular importance because of the high-resolution X-ray structure of the oxygen-evolving complex of photosystem II, which revealed a Lewis acidic Ca^{2+} ion intimately associated with the catalytic center in an Mn_4CaO_5 cluster.[1] Although mechanistic speculations suggest that the Ca^{2+} ion may interact directly with high-valent Mn–O species during the water oxidation process,[2] the role of this redox-inactive metal ion has yet to be clarified. In regard to the reactivity of Mn complexes with Lewis acids, an early study from Collins[3] provided the first and only example of the influence of redox-inactive metal ions on an isolable $Mn^{V}(O)$ compound, revealing enhanced reactivity of the $Mn^{V}(O)$ complex toward oxygen atom transfer (OAT). In this case the Lewis acids did not bind directly to the oxo ligand but rather to a secondary site incorporated in the tetraamide ligand. A dramatic acceleration in rates of oxidation of alkanes by addition of Lewis acids to MnO_4^- was demonstrated by Lau[4] and others.[5] More recently, Borovik reported that the rates of O_2 reduction by a Mn^{II} complex were accelerated by group 2 metal ions.[6] In related work, Fukuzumi and Nam provided some fundamental insights regarding the influence of Lewis acids on the electron-transfer (ET) and OAT reactivity of high-valent non-heme iron–oxo complexes.[7] An interesting example of a Cu^{2+} ion interacting with a $Cr^{V}(O)$ corrole was also described.[8] With the exception of the few former reports, much remains unknown about the reactivity of biologically relevant metal–oxo complexes with Lewis acids.

Herein we describe the influence of redox-inactive metal ions on an isolable $Mn^{V}(O)$ complex, $(TBP_8Cz)Mn^{V}(O)$ (TBP_8Cz = octakis(*p-tert*-butylphenyl)corrolazinato(3−)). We find that Zn^{2+} binds to the $Mn^{V}(O)$ complex with high affinity and induces interconversion of this complex to a valence tautomer characterized as a $Mn^{IV}(O)$ π-cation-radical (Scheme 1).

Scheme 1



Moreover, it is demonstrated that this chemically driven valence tautomerization is fully reversible and that the presence of the Lewis acidic Zn^{2+} ion has a dramatic effect on its ET and formal hydrogen-atom-transfer (HAT) reactivity.

Addition of $Zn(OTf)_2$ (1 equiv in 20 μL of CH_3CN) to a solution of $(TBP_8Cz)Mn^{V}(O)$ (16 μM) in CH_2Cl_2 at 23 °C resulted in a gradual color change over 1 h from bright green to brown. Monitoring this reaction by UV–vis spectroscopy revealed isosbestic conversion of the $Mn^{V}(O)$ complex (λ_{max}, nm (ε M^{-1} cm^{-1}): 419 (6.29×10^4), 634 (1.99×10^4)) to a new spectrum with peaks at 419 (3.97×10^4) and 789 (7.75×10^3) nm (Figure 1). Addition of excess Zn^{2+} (1–20 equiv) led to no further change in the UV–vis, and the final spectrum (λ_{max} = 789 nm) with 20 equiv of Zn^{2+} was stable at room temperature. The decrease and broadening of the Soret band at 419 nm, the loss of the Q-band at 634 nm, and the appearance of a weaker long-wavelength band at 789 nm are characteristic of the formation of a porphyrin or corrole π-cation radical.[9] In a previous report, we showed that reaction of $(TBP_8Cz)Mn^{V}(O)$ with one-electron oxidants (e.g., $Ar_3N^{+\bullet}$) resulted in the production of a π-cation-radical complex $[(TBP_8Cz^{+\bullet})Mn^{V}(O)]$, where the oxidizing equivalent mainly resides on the corrolazine ligand.[10] The spectrum of the oxidized complex (410, 780 nm) is strikingly similar to that seen for the product in the $Zn(OTf)_2$ reaction. These results suggested that addition of $Zn(OTf)_2$ caused the one-electron oxidation of (TBP_8Cz)-

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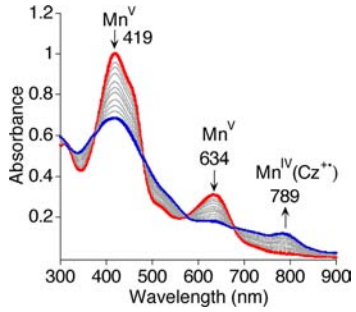


Figure 1. Time-resolved UV−vis spectra of $(TBP_8Cz)Mn^V(O)$ + $Zn(OTf)_2$ (1 equiv) for 1 h at 23 °C in CH_2Cl_2/CH_3CN (100:1 v:v).

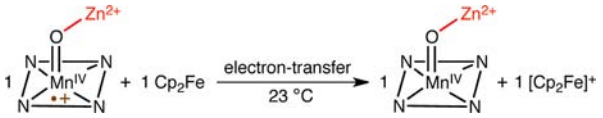
$Mn^V(O)$, but given that Zn^{2+} is redox-inactive, it was presumed that oxidation was a result of the aerobic reaction conditions. However, treatment of $(TBP_8Cz)Mn^V(O)$ with $Zn(OTf)_2$ under strictly air-free conditions did not change the outcome of this reaction (Figure S2). Addition of excess NaOTf (100 equiv) to the $Mn^V(O)$ complex also showed no change by UV−vis. This control experiment rules out coordination of OTf^- as the cause of the π-cation-radical formation and shows that the weaker Lewis acid Na^+ cannot substitute for Zn^{2+}.

^1H NMR spectroscopy of $(TBP_8Cz)Mn^V(O):Zn(OTf)_2$ (1:2) in CD_2Cl_2/CD_3CN revealed a paramagnetic spectrum (Figure S6), in stark contrast to the well-resolved diamagnetic spectrum seen for the starting low-spin d^2 $Mn^V(O)$ complex. With Zn^{2+}-facilitated oxidation ruled out, the paramagnetic NMR spectrum and UV−vis data suggested to us that perhaps Zn^{2+} coordination induces the interconversion of $(TBP_8Cz)Mn^V(O)$ with a valence tautomer, in which an electron from the Cz ring is transferred to Mn to give the electronic isomer $[(TBP_8Cz^{+\bullet})Mn^{IV}(O)-Zn^{2+}]$. Valence tautomerization is well documented in metalloporphyrins and metallocorroles[11] and has been proposed as playing a key role in the catalytic pathways of heme enzymes and porphyrin catalysts.[11a]

The proposed valence tautomer can be expected to exhibit a paramagnetic ground state, with a high-spin Mn^{IV} ($S = {}^3/_2$) ion either antiferromagnetically ($S_{total} = 1$) or ferromagnetically ($S_{total} = 2$) coupled to a Cz-based radical. An Evans method measurement gives $\mu_{eff} = 4.11$ μ_B, which falls between those predicted for $S = 1$ (2.83 μ_B) and $S = 2$ (4.90 μ_B). In fact, 4.11 μ_B is also quite close to the value predicted for non-interacting *hs*-Mn^{IV} and $Cz^{+\bullet}$ centers (4.24 μ_B). For comparison, the nature and extent of the magnetic coupling in $Mn^{III}(porph^{+\bullet})$ complexes has led to conflicting interpretations that include both coupled and uncoupled descriptions.[12] X-band EPR spectroscopy of $[(TBP_8Cz^{+\bullet})Mn^{IV}(O)-Zn^{2+}]$ at 77 K revealed that the compound was EPR silent, consistent with an integer-spin Mn^{IV} π-cation-radical complex. An unambiguous assignment of the coupling in $[(TBP_8Cz^{+\bullet})Mn^{IV}(O)-Zn^{2+}]$ cannot be made at this time. However, taken together, the magnetic data provide strong evidence for the conclusion that a Mn^{IV} π-cation-radical complex is generated upon addition of Zn^{2+} ions.

The ET properties of $[(TBP_8Cz^{+\bullet})Mn^{IV}(O)-Zn^{2+}]$ were next investigated, providing further insights into the nature of this species and revealing some novel ET behavior not seen previously for the $Mn^V(O)$ starting material. The redox potential for the $Mn^V(O)$ complex (0.02 V vs SCE)[13] predicts that the driving force for one-electron reduction by ferrocene (Fc) (0.37 V vs SCE) is significantly uphill ($\Delta G_{et} = 0.35$ eV). Experimental verification of this prediction has been made, where no reaction is observed between $(TBP_8Cz)Mn^V(O)$ and Fc, and only more strongly reducing Fc derivatives (e.g., $[Fe(C_5HMe_4)_2]$, $E_{ox} = -0.04$ V vs SCE) react with the $Mn^V(O)$ complex ($k_{et} = (7.5 \pm 0.4) \times 10^4$ M^{-1} s^{-1}).[14] In contrast, titration of a solution of $(TBP_8Cz)Mn^V(O):Zn(OTf)_2$ (1:20) with Fc leads to a rapid reaction, resulting in the characteristic spectrum for a Mn^{IV} complex and closed-shell Cz ring, $[(TBP_8Cz)Mn^{IV}]^+$ (443, 724 nm)[14] (Scheme 2). The

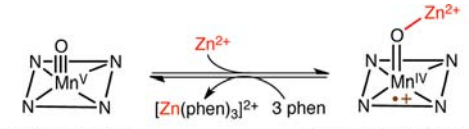
Scheme 2



stoichiometry of the ET reaction was confirmed to be 1:1 (Figure S9). Our previous attempts to reduce the $(TBP_8Cz)Mn^V(O)$ complex with Fc derivatives resulted in direct two-electron reduction to give $(TBP_8Cz)Mn^{III}$, with no observable Mn^{IV} intermediate. The $[(TBP_8Cz)Mn^{IV}]^+$ complex was only successfully characterized under *oxidizing* conditions, in which $(Cz)Mn^{III}$ was treated with strong one-electron oxidants.[14] The ET properties of the $[(TBP_8Cz^{+\bullet})Mn^{IV}(O)-Zn^{2+}]$ complex are fully consistent with the valence tautomer assignment and indicate that $[(TBP_8Cz^{+\bullet})Mn^{IV}(O)-Zn^{2+}]$ has a significantly higher redox potential than the starting Mn^V valence tautomer.

Efficient sequestration of the Zn^{2+} ions leads to regeneration of the starting $(TBP_8Cz)Mn^V(O)$ complex. Addition of excess 1,10-phenanthroline, a strong Zn^{2+} chelator, to a solution of $(TBP_8Cz)Mn^V(O):Zn(OTf)_2$ (1:1) caused the immediate reversion of the π-cation-radical spectrum back to that of the starting $Mn^V(O)$ complex (Scheme 3, Figure 2a). Control

Scheme 3. Chelation of Zn^{2+} by 1,10-Phenanthroline (phen)



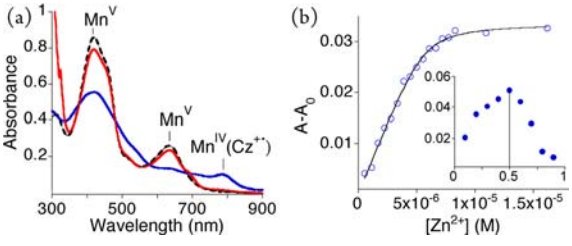


Figure 2. (a) UV−vis spectra of $(TBP_8Cz)Mn^V(O)$ (dashed line), $[(TBP_8Cz^{+\bullet})Mn^{IV}(O)-Zn^{2+}]$ (blue line), and after addition of 1,10-phenanthroline (30 equiv) (red line). (b) Binding isotherm (plotted at 789 nm) for the addition of $Zn(OTf)_2$. Inset: Job's plot ($x = [Zn^{2+}]/([Zn^{2+}] + [(TBP_8Cz)Mn^V(O)])$, $y = A - A_0$).

reactions performed by adding $[Zn(phen)_3]^{2+}$ to $(TBP_8Cz)Mn^V(O)$ did not result in any change by UV−vis, confirming that "free" Zn^{2+} is required to bind $(TBP_8Cz)Mn^V(O)$ in order to observe the conversion. Spectral titration of $(TBP_8Cz)Mn^V(O)$ with $Zn(OTf)_2$ results in a binding isotherm for Zn^{2+}, as shown in Figure 2b. This curve can be fit by a 1:1 binding model, which yields an association constant for Zn^{2+} of $K_a = 4.03 \times 10^6$ M^{-1}. A Job's plot (Figure 2b, inset) reaches a

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maximum at a molar ratio of 0.5, confirming a 1:1 binding stoichiometry. The relatively high K_a obtained from the binding curve indicates a surprisingly strong interaction between the $Mn^{V}(O)$ complex and the Lewis acidic Zn^{2+} ion, but one which is fully reversible upon chelation with 1,10-phenanthroline.

The reversible interconversion of valence tautomers is a highly desirable feature for their potential use in electronic devices and other related applications. A well-known example of chemically driven valence tautomerization is the addition of strong axial donors (e.g., OR^-) to $Mn^{III}(porph^{+\bullet})$ complexes, which induces their conversion to $Mn^{IV}(porph)$.[11d] Mn-salen complexes have exhibited acid-dependent valence tautomerization.[15] However, the reversibility of these processes has not been demonstrated. Metal complexes and redox-active ligands, including both non-porphyrin (e.g., quinonoid-M^{n+}) and porphyrin complexes, have exhibited reversible valence tautomer behavior, but these systems typically respond to temperature, pH, or pressure changes to control the interconversion.[11b,16] The Zn^{2+}-induced interconversion described here is, to our knowledge, the first example (outside systems that respond to pH) of a *well-defined chemically driven reversible valence tautomerization*. These results provide motivation for the future design of valence tautomers that respond to chemical stimuli.

To gain further insight we performed density functional theory (DFT) calculations[17] on a simplified $[(H_8Cz)Mn(O)-Zn^{2+}]$ model where the eight TBP groups were replaced by H-atoms. Full geometry optimizations of the structures were done in a dielectric constant of $\varepsilon = 5.7$. The optimized geometry for $[(H_8Cz)Mn(O)-Zn^{2+}]$ (Figure 3) has close-lying triplet and

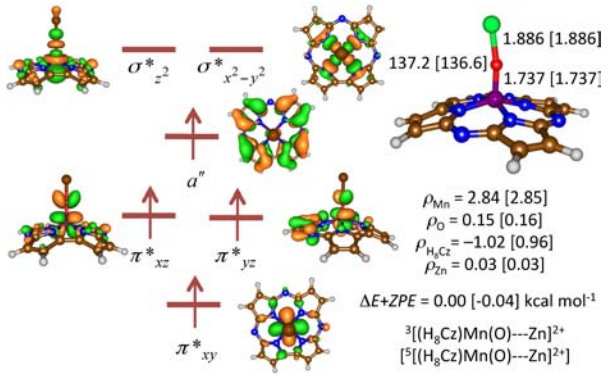


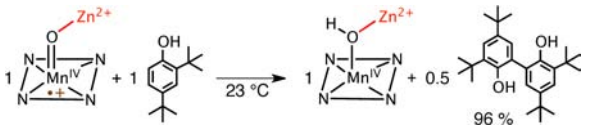
Figure 3. Frontier molecular orbitals and optimized geometries of $^{3,5}[(H_8Cz^{+\bullet})Mn^{IV}(O)-Zn^{2+}]$ in a dielectric constant of $\varepsilon = 5.7$. Bond lengths in Å, angles in deg, and spin densities (ρ) in au.

quintet spin states with $\pi^*_{xy}{}^1\,\pi^*_{xz}{}^1\,\pi^*_{yz}{}^1\,a''^1$ occupation, where the H_8Cz π-orbital is either antiferromagnetically or ferromagnetically coupled to the unpaired electrons on the manganese. This configuration resembles the electronic state of Compound I of cytochrome P450, where metal-based π^* orbitals couple to a porphyrin radical.[18] The Mn−O bond distance of 1.737 Å is considerably elongated compared to the triple bond in $(TBP_8Cz)Mn^{V}(O)$ (1.56 Å),[13] while the Zn−O bond is rather short (1.886 Å) and implies significant bonding character between the two atoms. For comparison, an oxo-bridged $Zn^{2+}-O-Zn^{2+}$ complex shows Zn−O = 1.854(1) Å.[19] Thus, the DFT-optimized structure predicts a tight bonding interaction between Mn(O) and Zn^{2+}, providing a theoretical underpinning for the large K_a value. This result is similar to that seen for a non-heme Fe(O)---Sc^{3+} complex, which exhibits elongated Fe−O and short Sc^{3+}−O bonds.[7a]

The frontier molecular orbitals for the close-lying triplet and quintet states are shown in Figure 3. The lengthening of the Mn−O distance and disruption of the π donor ability of the oxo ligand bring the vacant π^*(Mn−O) orbitals down in energy (Table S5), allowing for an electron to be transferred from the Cz-based *a″* orbital into the vacant π^*_{yz} molecular orbital to give an Mn^{IV} center. At the same time, one of the π^*_{xy} electrons is promoted to π^*_{xz}, giving an $S = {}^3/_2$ spin state on Mn^{IV} coupled to an $S = {}^1/_2$ spin state on H_8Cz. DFT calculations on the alternative $[(H_8Cz)Mn^{V}(O)-Zn^{2+}]$ singlet state locate it at $\Delta E + ZPE = 24.6$ kcal mol^{-1} above the triplet spin ground state. Overall, the DFT calculations are in excellent agreement with the conclusion that binding of Zn^{2+} causes interconversion to the valence tautomer $[(TBP_8Cz^{+\bullet})Mn^{IV}(O)-Zn^{2+}]$.

Preliminary examination of the reactivity of the Mn−oxo complex in the presence of Zn^{2+} with substituted phenol substrates reveals a significant influence of the Zn^{2+} ion on HAT. Treatment of $(TBP_8Cz)Mn^{V}(O):Zn(OTf)_2$ (1:1) with 2,4-di-*tert*-butylphenol (5.0 equiv) at 23 °C led to the formation of $[(TBP_8Cz)Mn^{IV}]^+$, as indicated by UV−vis. Product analysis by GC-FID showed the production of bis(phenol) dimer in high yield (96%) according to the stoichiometry in Scheme 4, with unreacted phenol accounting

Scheme 4



for the mass balance. This result is in agreement with the ET reactivity involving Fc, where $[(TBP_8Cz^{+\bullet})Mn^{IV}(O)-Zn^{2+}]$ acts as a one-electron oxidant. In contrast, $(TBP_8Cz)Mn^{V}(O)$ functions only as a two-electron oxidant toward both phenols[20] and C−H substrates.[21] Interestingly, our results are opposite to those found for $[(TMC)Fe^{IV}(O)]^{2+}$, for which it was shown that binding of Ca^{2+} and Sc^{3+} led to a two-electron reduction by Cp_2Fe as opposed to a one-electron process in the absence of redox-inactive metals.[7a]

Reaction rates were measured for the reaction of $[(TBP_8Cz^{+\bullet})Mn^{IV}(O)-Zn^{2+}]$ with excess 2,4,6-tri-*tert*-butylphenol, and the resulting k_{obs} values correlated linearly with substrate concentration (Figure 4). A second-order rate constant of $k'' = 0.25 \pm 0.02$ M^{-1} s^{-1} was obtained, whereas

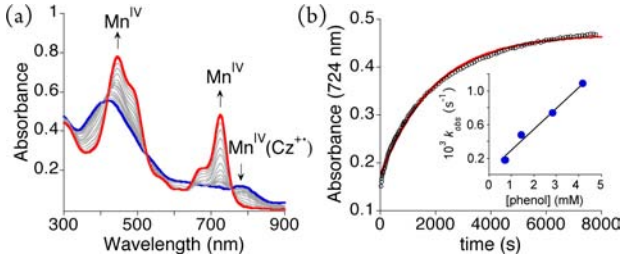


Figure 4. (a) Time-resolved UV−vis spectra of $[(TBP_8Cz^{+\bullet})Mn^{IV}(O)-Zn^{2+}]$ + 2,4,6-di-*tert*-butylphenol (100 equiv) at 23 °C. (b) Change in absorbance at 724 nm vs time corresponding to the formation of $[(TBP_8Cz)Mn^{IV}]^+$ (black circles) and best fit (red line). Inset: second-order rate plot.

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in the absence of Zn^{2+}, $k'' = 0.074 \pm 0.007\ M^{-1}\ s^{-1}$ for the same substrate.[20] Thus there is a modest rate enhancement of ~3-fold in the presence of the Zn^{2+} ion. Although this rate enhancement is not dramatic, it may be caused by the stabilization of the exchange-enhanced triplet state in $[(TBP_8Cz^{+\bullet})Mn^{IV}(O)-Zn^{2+}]$. Early work on the reactivity of non-heme iron(IV)−oxo complexes pointed to exchange-enhanced reactivity whereby high-spin states react faster than low-spin states.[22] Also, the nature of the Lewis acid and substrates employed may play a key role in determining the overall effect on reaction rates.

In conclusion, we have described the first examination of the influence of a Lewis acid on the properties and reactivity of a high-valent Mn−oxo porphyrinoid complex. We also have demonstrated the first example of a chemically driven, reversible valence tautomerization between a metal ion and a redox-active ligand. The influence of the Lewis acidic Zn^{2+} on the $Mn^{V}(O)$ complex is analogous to the effect of H^+ on His-ligated ferryl heme as shown by Gray and co-workers, where protonation of the terminal oxo ligand causes an intramolecular electron transfer to give a ferric porphyrin π-cation-radical.[16d] In contrast, protonation of the ferryl intermediate (Compound II) in Cytochrome P450 (Cyt-P450) does not result in a conversion to the Fe^{III} π-cation-radical but rather leaves the high-valent Fe^{IV} state intact.[23] The Cz ligand has a high propensity for stabilizing high-valent states but cannot maintain the Mn^{V} state upon metalation of the oxo donor. Thus our results, together with the influence of H^+ on His-ligated ferryl hemes, suggest that the strong donation from the unique thiolate ligand in Cyt-P450 may play an important role in stabilizing the high-valent metal ion in Compound II.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, spectroscopic data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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