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Tuning the Redox Properties of a Nonheme Iron(III)–Peroxo Complex Binding Redox-Inactive Zinc Ions by Water Molecules

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Abstract

Redox-inactive metal ions play important roles in tuning chemical properties of metal–oxygen intermediates. Herein we report the effect of water molecules on the redox properties of a nonheme iron(III)–peroxo complex binding redox-inactive metal ions. The coordination of two water molecules to a Zn^{2+} ion in $(\text{TMC})\text{Fe}^{\text{III}}-(\text{O}_2)-\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (**1**- Zn^{2+}) decreases the Lewis acidity of the Zn^{2+} ion, resulting in the decrease of the one-electron oxidation and reduction potentials of **1**- Zn^{2+} . This further changes the reactivities of **1**- Zn^{2+} in oxidation and reduction reactions; no reaction occurred upon addition of an oxidant (e.g., cerium(IV) ammonium nitrate (CAN)) to **1**- Zn^{2+} , whereas **1**- Zn^{2+} coordinating two water molecules, $(\text{TMC})\text{Fe}^{\text{III}}-(\text{O}_2)-\text{Zn}(\text{CF}_3\text{SO}_3)_2-(\text{OH}_2)_2$ [**1**- $\text{Zn}^{2+}-(\text{OH}_2)_2$], releases the O_2 unit in the oxidation reaction. In the reduction reactions, **1**- Zn^{2+} was converted to its corresponding iron(IV)–oxo species upon addition of a reductant (e.g., a ferrocene derivative), whereas such a reaction occurred at a much slower rate in the case of **1**- $\text{Zn}^{2+}-(\text{OH}_2)_2$. The present results provide the first biomimetic example showing that water molecules at the active sites of metalloenzymes may participate in tuning the redox properties of metal–oxygen intermediates.

Keywords

bioinorganic chemistry; metal–oxygen intermediates; oxygen-evolving complexes; redox reactions; water oxidation

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There is much current interest in understanding the roles of redox-inactive metal ions in modulating reactivities of metal–oxygen intermediates in enzymatic and biomimetic reactions. For example, a redox-inactive Ca^{2+} ion is required to produce O_2 at the oxygen-evolving complex (OEC) of photosystem II (PSII).^[1–3] In the reactions of high-valent metal–oxo complexes, the stabilities and reactivities of iron(IV)–, manganese(IV or V)–, and cobalt(IV)–oxo complexes are markedly affected by binding redox-inactive metal ions (e.g., Sc^{3+} ion).^[4–6] In O_2 -activation reactions, Borovik and co-workers demonstrated that the redox-inactive metal ions accelerate the reduction of O_2 by iron(II) and manganese(II) complexes.^[7]

Very recently, nonheme iron(III)–peroxo complexes binding redox-inactive metal ions, $[(\text{TMC})\text{Fe}^{\text{III}}(\text{O}_2)]^+-\text{M}^{n+}$ ($\mathbf{1-M}^{n+}$; $\text{M}^{n+} = \text{Sr}^{2+}, \text{Ca}^{2+}, \text{Zn}^{2+}, \text{Lu}^{3+}, \text{Y}^{3+}$, and Sc^{3+}), were successfully synthesized by reacting a nonheme iron(III)–peroxo complex, $[(\text{TMC})\text{Fe}^{\text{III}}(\text{O}_2)]^+ (\mathbf{1})$,^[8] with various redox-inactive metal ions.^[9, 10] The Lewis acidity of the redox-inactive metal ions was shown to be an important factor that determines the redox potentials and reactivities of $\mathbf{1-M}^{n+}$ with electron donors and acceptors.^[9b] For example, as the Lewis acidity of the redox-inactive metal ions increased, the one-electron oxidation and reduction potentials of $\mathbf{1-M}^{n+}$ became more positive. Further, the $\mathbf{1-M}^{n+}$ complexes binding Ca^{2+} and Sr^{2+} ions showed similar redox potentials and reactivities in the one-electron oxidation and reduction reactions. Furthermore, the $\mathbf{1-M}^{n+}$ complexes binding Ca^{2+} and Sr^{2+} ions were oxidized by an oxidant [e.g., cerium(IV) ammonium nitrate (CAN)] to release O_2 , whereas no release of O_2 occurred for complexes binding stronger Lewis acids ($\mathbf{1-M}^{n+}$; $\text{M}^{n+} = \text{Zn}^{2+}, \text{Lu}^{3+}, \text{Y}^{3+}$, and Sc^{3+}).^[9b]

Water molecules at the active sites of metalloenzymes play a vital role in shaping their structures and functions.^[11] Recently, the crystal structure of the OEC in PSII shows the presence of water molecules near the Ca^{2+} ion in the OEC.^[1f] In addition, it has been shown that the Lewis acidity of redox-inactive metal ions decreases by coordinating water molecules.^[12] Therefore, we were curious about the effect of water molecules on the redox properties of metal–dioxygen intermediates binding redox-inactive metal ions. Herein we report for the first time the synthesis of a nonheme iron(III)–peroxo–zinc(II) complex coordinating two water molecules, $(\text{TMC})\text{Fe}^{\text{III}}-(\text{O}_2)-\text{Zn}^{2+}-(\text{OH}_2)_2 [\mathbf{1-Zn}^{2+}-(\text{OH}_2)_2]$ (Figure 1), and the effect of the water coordination on the Lewis acidity of the Zn^{2+} ion and the redox properties and reactivities of the iron(III)–peroxo complex binding zinc(II) ion, $(\text{TMC})\text{Fe}^{\text{III}}-(\text{O}_2)-\text{Zn}^{2+} (\mathbf{1-Zn}^{2+})$, Scheme 1).

An iron(III)–peroxo complex binding Zn^{2+} ion ($\mathbf{1-Zn}^{2+}$) was prepared by adding Zn^{2+} ion (50 mM) to $[(\text{TMC})\text{Fe}^{\text{III}}(\text{O}_2)]^+ (\mathbf{1})$.^[8, 9b] Upon addition of H_2O (0–2.8M) to a solution of $\mathbf{1-Zn}^{2+}$ in CH_3CN (MeCN) at 273 K, the absorption band at 650 nm for $\mathbf{1-Zn}^{2+}$ was red-shifted to 760 nm with a clean isosbestic point at 765 nm, and the shift of the absorption band was found to depend on the amount of H_2O added (Figure 2a). The spectral change of $\mathbf{1-Zn}^{2+}$ exhibits a sigmoidal curvature (Figure 2b), suggesting that more than one H_2O molecule is coordinated to $\mathbf{1-Zn}^{2+}$. The observation of the clean isosbestic point indicates that there is an equilibrium between $\mathbf{1-Zn}^{2+}$ and $\mathbf{1-Zn}^{2+}$ binding water molecules. In such a case, the absorption change (ΔA) at 650 nm due to the formation of $\mathbf{1-Zn}^{2+}$ species binding H_2O is given by Equation (1),

$$\Delta A = \Delta A_0 / (1 + K[\text{H}_2\text{O}]^n) \quad (1)$$

where A_0 is the final absorption change, n is the number of H_2O molecules coordinated to Zn^{2+} ion, and K is the formation constant. The number of H_2O molecules bound and the formation constant were determined to be 2 and $1.9(1) \text{ M}^{-2}$ at 273 K, respectively (see Figure S1 in the Supporting Information for the detailed calculation method). This indicates that two H_2O molecules are coordinated to the Zn^{2+} ion to form $[(\text{TMC})\text{Fe}^{\text{III}}(\text{O}_2)]^+ \cdot \text{Zn}^{2+} \cdot (\text{OH}_2)_2$ [$\mathbf{1}\text{-Zn}^{2+} \cdot (\text{OH}_2)_2$] (Scheme 1; Figure 1 for DFT-optimized structure; Experimental Section for DFT calculations and Tables S1–S3 in the Supporting Information). In the case of the $\mathbf{1}\text{-Ca}^{2+}$ complex, a similar trend of red-shift of absorption band was observed (see Figure S2 in the Supporting Information). In the presence of Ca^{2+} ions (50 mM), the number of H_2O molecules bound to $\mathbf{1}\text{-Ca}^{2+}$ and the formation constant of $\mathbf{1}\text{-Ca}^{2+} \cdot (\text{OH}_2)_2$ were determined to be 2 and $0.52(3) \text{ M}^{-2}$ at 273 K, respectively (see Figures S2 and S3 in the Supporting Information). However, in the case of Fe^{III} -peroxo complexes binding redox-inactive metal ions with a stronger Lewis acidity than Zn^{2+} ion (i.e., $\mathbf{1}\text{-Sc}^{3+}$), addition of H_2O to a solution of $\mathbf{1}\text{-Sc}^{3+}$ resulted in the disappearance of the absorption band at 530 nm due to $\mathbf{1}\text{-Sc}^{3+}$, accompanied by the appearance of an absorption band at 810 nm due to $\mathbf{1}$ (see Figure S4a in the Supporting Information), indicating that Sc^{3+} ion was released from the Fe^{III} -peroxo moiety in the presence of a large concentration of H_2O .

The EPR spectrum of $\mathbf{1}\text{-Zn}^{2+} \cdot (\text{OH}_2)_2$ exhibits signals at $g = 9.4$ and 4.3 (see Figure S5 in the Supporting Information), which is indicative of high-spin ($S = 5/2$) Fe^{III} species. It is worth noting that the EPR feature of $\mathbf{1}\text{-Zn}^{2+} \cdot (\text{OH}_2)_2$ is completely different from those of $\mathbf{1}^{[8]}$ and $\mathbf{1}\text{-Zn}^{2+[9b]}$ but similar to that of $\mathbf{1}\text{-Sr}^{2+}$ (see Figure S5 in the Supporting Information). The binding of Zn^{2+} ion to $\mathbf{1}$ in the absence and presence of H_2O molecules was also confirmed by recording a coldspray ionization time-of-flight mass (CSI-TOF MS) spectrum of $\mathbf{1}\text{-Zn}^{2+}$ (see Figure S6 in the Supporting Information). However, H_2O molecules in the $\mathbf{1}\text{-Zn}^{2+} \cdot (\text{OH}_2)_2$ species were not detected under the CSI-TOF MS conditions.

It has been shown that the Lewis acidity of metal ions can be quantitatively determined from the g_{zz} values of EPR spectra of $\text{O}_2^{\bullet-}$ -metal ion complexes,^[13] since the g_{zz} values decrease with the increase of the Lewis acidity of metal ions according to Equation (2),

$$g_{zz} = g_e + \lambda / \Delta E \quad (2)$$

where g_e ($= 2.0023$) is the g value of free spin, λ ($= 0.014 \text{ eV}$) is the spin-orbit coupling constant of oxygen, and E is the energy splitting value of the π_g orbital due to the binding of metal ions to $\text{O}_2^{\bullet-}$, which can be used as a quantitative measure of the Lewis acidity of metal ions.^[13, 14] The Lewis acidity of the Zn^{2+} ion in the presence of 1.4 M of H_2O was determined to be $(0.57 \pm 0.01) \text{ eV}$ from the E value (see Figure S7 in the Supporting Information),^[9b, 13] which is between the E value of the Ca^{2+} ion (0.58 eV) and the Sr^{2+} ion (0.53 eV ; vide infra). We thus conclude that the Lewis acidity of the Zn^{2+} ion in $\mathbf{1}\text{-Zn}^{2+}$ decreases by coordinating water molecules (Scheme 1, note 1) and that the Lewis acidity of Zn^{2+} in $\mathbf{1}\text{-Zn}^{2+} \cdot (\text{OH}_2)_2$ is similar to those of metal ions in $\mathbf{1}\text{-Ca}^{2+}$ and $\mathbf{1}\text{-Sr}^{2+}$; the Lewis acidities of the metal ions in the latter species are shown to be similar.^[9b] The decrease of

Lewis acidity of metal ion upon addition of water was also confirmed by the fluorescence spectral change of the acridone/ Zn^{2+} complex (see Figures S8–S10 in the Supporting Information). The fluorescence maximum of the acridone/ Zn^{2+} complex is blue-shifted with increasing concentration of water to that of the acridone/ $\text{Zn}^{2+}-(\text{OH}_2)_2$ complex, which is similar to that of the acridone- Sr^{2+} complex (see Figure S9 in the Supporting Information). In addition, the fluorescence maximum did not return back to that of free acridone, being consistent with the result of UV/Vis titration (see Figure 2).

We then investigated the electrochemical oxidation of $\mathbf{1}\text{-Zn}^{2+}$ by varying the amounts of H_2O added to the solution of $\mathbf{1}\text{-Zn}^{2+}$ (Figure 3a). As shown in the cyclic voltammogram of $\mathbf{1}\text{-Zn}^{2+}$ in the one-electron oxidation process (black line), no oxidation peak was observed up to 1.7 V versus SCE.^[9b] In the presence of 0.28_M of H_2O , however, the anodic current peak (E_{pa}) due to the oxidation of $\mathbf{1}\text{-Zn}^{2+}$ was observed at 1.45 V versus SCE (pink line in Figure 3a). No corresponding cathodic current peak (E_{pc}) was observed at the reverse scan due to the release of O_2 upon the one-electron oxidation.^[9b] In the presence of 0.70_M of H_2O , the E_{pa} value of $\mathbf{1}\text{-Zn}^{2+}$ was significantly shifted to the negative direction (blue line in Figure 3a; $E_{\text{pa}} = 1.06$ V vs. SCE). The E_{pa} value was further shifted to the negative direction upon addition of 1.4 and 2.8_M of H_2O (red and green lines in Figure 3a; $E_{\text{pa}} = 0.95$ and 0.93 V vs. SCE), and these values are nearly the same as those of $\mathbf{1}\text{-Ca}^{2+}$ ($E_{\text{pa}} = 0.96$ V vs. SCE) and $\mathbf{1}\text{-Sr}^{2+}$ ($E_{\text{pa}} = 0.94$ V vs. SCE).^[9b] In the presence of > 2.8_M of H_2O , no further shift of the E_{pa} value was observed.

In the case of the one-electron reduction process of $\mathbf{1}\text{-Zn}^{2+}$, the cathodic current peak (E_{pc}) due to the reduction of $\mathbf{1}\text{-Zn}^{2+}$ was observed at -0.16 V versus SCE in the absence of H_2O (Figure 3b, black line),^[9b] but no corresponding anodic current peak (E_{pa}) was observed at the reverse scan due to the O–O bond cleavage of the one-electron reduced species, which resulted in the formation of the corresponding iron(IV)–oxo species, $[(\text{TMC})\text{Fe}^{\text{IV}}(\text{O})]^{2+}$ ($\mathbf{2}$).^[9, 10] In the presence of 0.70_M of H_2O , the E_{pc} value was shifted to the negative direction (blue line in Figure 3b; $E_{\text{pc}} = -0.31$ V vs. SCE). The E_{pc} values in the presence of 1.4 and 2.8_M of H_2O ($E_{\text{pc}} = -0.38$ V vs. SCE) were further shifted to the negative direction (red line in Figure 3b and Figure S11 in the Supporting Information for 1.4 and 2.8_M of H_2O , respectively). These results clearly indicate that the one-electron oxidation and reduction potentials of $\mathbf{1}\text{-Zn}^{2+}$ decrease as the amount of added H_2O increases (Scheme 1, note 2). Moreover, the oxidation and reduction potentials of $\mathbf{1}\text{-Zn}^{2+}-(\text{OH}_2)_2$ are similar to those of $\mathbf{1}\text{-Ca}^{2+}$ and $\mathbf{1}\text{-Sr}^{2+}$.^[9b]

The electron-transfer oxidation of $\mathbf{1}\text{-Zn}^{2+}$ in the absence and presence of H_2O was examined by using CAN as an oxidant. Addition of one equivalent of CAN to the solution of $\mathbf{1}\text{-Zn}^{2+}$ resulted in the immediate disappearance of the absorption band at 650 nm due to $\mathbf{1}\text{-Zn}^{2+}$ with the concomitant appearance of the absorption band at 585 nm (see Figure S12 in the Supporting Information). In this reaction, no release of O_2 was detected by GC and mass spectrometry, as reported previously in the reactions of $\mathbf{1}\text{-M}^{n+}$ ($\text{M}^{n+} = \text{Zn}^{2+}$, Lu^{3+} , Y^{3+} , and Sc^{3+}) with CAN.^[9b] We may assign the new species with an absorption band at 585 nm as a cerium(IV) ion-bound iron(III)–peroxo species ($\mathbf{1}\text{-Ce}^{4+}$); we have shown previously that the

Zn^{2+} ion in $\mathbf{1}\text{-Zn}^{2+}$ can be replaced by redox-inactive metal ions with a greater Lewis acidity and the Lewis acidity of the Ce^{4+} ion is higher than that of the Zn^{2+} ion.^[9b]

In sharp contrast to the result of $\mathbf{1}\text{-Zn}^{2+}$ (i.e., no H_2O added), addition of one equivalent of CAN to the solution of $\mathbf{1}\text{-Zn}^{2+}\text{-(OH}_2)_2$, which was prepared by adding 1.4_M of H_2O to $\mathbf{1}\text{-Zn}^{2+}$, caused the immediate disappearance of the absorption band at (715±5) nm due to $\mathbf{1}\text{-Zn}^{2+}\text{-(OH}_2)_2$ (Figure 4a). The analysis of the reaction solution revealed the formation of $[(\text{TMC})\text{Fe}^{\text{II}}]^{2+}$ species by EPR and electrospray ionization mass spectrometry (ESI MS; see Figure S13 in the Supporting Information).^[9b] In this case, the release of O_2 was detected by GC and mass spectrometry ((83±5)% yield based on $\mathbf{1}\text{-Zn}^{2+}$ used; see Experimental Section in the Supporting Information), showing that $\mathbf{1}\text{-Zn}^{2+}\text{-(OH}_2)_2$ was oxidized by CAN to produce O_2 and the Fe^{II} complex, as reported previously in the reactions of $\mathbf{1}\text{-Ca}^{2+}$ and $\mathbf{1}\text{-Sr}^{2+}$.^[9b] To confirm the source of O_2 , ^{18}O -labeled $\mathbf{1}\text{-Zn}^{2+}\text{-(OH}_2)_2$ complex was prepared and allowed to react with CAN. The resulting mass spectra in Figure 4b clearly show the evolution of $^{18}\text{O}_2$, demonstrating unambiguously that the ^{18}O -labeled $\mathbf{1}\text{-Zn}^{2+}\text{-(OH}_2)_2$ complex released its binding $^{18}\text{O}_2$ by the oxidation with CAN (Scheme 1, note 3).

The electron-transfer reduction of $\mathbf{1}\text{-Zn}^{2+}$ in the absence and presence of H_2O was also examined by using 1,1'-dimethylferrocene (Me_2Fc) as a reductant. Electron transfer from Me_2Fc to $\mathbf{1}\text{-Zn}^{2+}$ in the absence of H_2O resulted in the formation of $[(\text{TMC})\text{Fe}^{\text{IV}}(\text{O})]^{2+}$ (**2**) via heterolytic O–O bond cleavage of the peroxide ligand (see Figure S14 in the Supporting Information).^[9, 10, 15] The rate of electron transfer obeyed first-order kinetics and the pseudo-first-order rate constant increased linearly with the increase of the Me_2Fc concentration. The second-order rate constant (k_{et}) of electron transfer was determined to be 23(2) $\text{M}^{-1} \text{s}^{-1}$ (see Figure S14a in the Supporting Information). The k_{et} value decreased with increasing the H_2O concentration (Figure 5 and Figure S15 in the Supporting Information);^[9] the k^{et} value determined in the presence of 2.8_M of H_2O was approximately 50 times smaller than that determined in the absence of H_2O . It should be noted that no reaction between **1** and Me_2Fc occurred without Zn^{2+} ion in the absence and presence of H_2O . These results clearly indicate that the rate of the one-electron reduction of $\mathbf{1}\text{-Zn}^{2+}$ depends on the H_2O concentration in solution. These results are also in line with our previous observation that the one-electron reduction of $\mathbf{1}\text{-M}^{n+}$ depends on the Lewis acidity of the M^{n+} ion;^[9b] the O–O bond cleavage of $\mathbf{1}\text{-Zn}^{2+}$ slows down as the Lewis acidity of the Zn^{2+} ion in $\mathbf{1}\text{-Zn}^{2+}$ decreases by coordinating water molecules (Scheme 1, note 4).

In conclusion, we have demonstrated the significant effect of water molecules on the redox properties and reactivities of a nonheme iron(III)–peroxo complex binding redox-inactive Zn^{2+} ion ($\mathbf{1}\text{-Zn}^{2+}$; Scheme 1). We have interpreted these results with the change of the Lewis acidity of the Zn^{2+} ion owing to the coordination of water molecules to the Zn^{2+} ion in $\mathbf{1}\text{-Zn}^{2+}$. The present results suggest that water molecules at the active sites of metalloenzymes play important roles in fine-tuning of the redox properties of metal–oxygen intermediates.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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Figure 1. DFT-optimized structure of **1**-Zn²⁺ binding two water molecules, (TMC)Fe^{III}-(O₂)-Zn(CF₃SO₃)₂-(OH₂)₂ [**1**-Zn²⁺-(OH₂)₂] (color code: Fe, orange; Zn, green; N, blue; O, red; S, yellow; C, gray; F, pink) with the distances [Å] of Fe-Zn and Zn-O bonds. The values in parenthesis are the distances [Å] in the absence of water. Blue dotted lines show the hydrogen bonding interaction.

Figure 2.

a) Absorption spectral changes of **1**-Zn²⁺ (0.50 mM; blue line) upon addition of H₂O (0–2.8 M with interval of 0.28 M) in the presence of Zn²⁺ ions (50 mM) in MeCN at 273 K. b) Plot of absorbance at 650 nm against concentration of H₂O in MeCN at 273 K. Red line shows the fitting line, which is drawn using Equation (1); where $n = 2$ and $K = 1.9 \text{ M}^{-2}$.

Figure 3.

Cyclic voltammograms of 1-Zn^{2+} in the absence (black lines) and presence of H_2O [0.28_M (pink), 0.70_M (blue), 1.4_M (red), and 2.8_M (green)] in one-electron oxidation (a) and one-electron reduction (b) processes in MeCN at 273 K.

Figure 4.

a) Absorption spectral change observed in the reaction of $1\text{-Zn}^{2+}\text{-(OH}_2)_2$ (0.50 mM) and CAN (0.50 mM; 1.0 equiv) in the presence of H_2O (1.4_M) in MeCN at 253 K. Absorption band at 715 nm (red line) due to $1\text{-Zn}^{2+}\text{-(OH}_2)_2$ (i.e., in the presence of 1.4_M of H_2O) was decayed to black line upon addition of CAN in MeCN at 253 K. b) Mass spectra monitoring O_2 isotopes [32 ($^{16}\text{O}-^{16}\text{O}$; black circles), 34 ($^{16}\text{O}-^{18}\text{O}$; blue circles), and 36 ($^{18}\text{O}-^{18}\text{O}$; red circles)] produced in the reactions of ^{18}O -labeled $[(\text{TMC})\text{Fe}^{\text{III}}(^{18}\text{O}_2)]^+-\text{Zn}^{2+}$ (0.25 mM) with CAN (0.25 mM) in the presence of H_2O (1.4_M) in MeCN at 253 K.

Figure 5.
Plot of k_{et} against concentration of H_2O in electron transfer from Me_2Fc to $1-Zn^{2+}$ (0.50 mM) in the absence and presence of H_2O (0M, 0.56M, 1.1M, 1.7M, 2.2M and 2.8M) in MeCN at 273 K.

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1. Decrease of Lewis acidity of Zn^{2+} ion
 2. Decrease of oxidation and reduction potentials
 3. Increase of reactivity in oxidation reaction
 4. Decrease of reactivity in reduction reaction

Scheme 1.

Effects of water coordination to Zn^{2+} ion in $\mathbf{1-Zn}^{2+}$.