

# The Effects of Redox-Inactive Metal Ions on the Activation of Dioxygen: Isolation and Characterization of a Heterobimetallic Complex Containing a $\text{Mn}^{\text{III}}-(\mu\text{-OH})-\text{Ca}^{\text{II}}$ Core

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**S** Supporting Information

**ABSTRACT:** Rate enhancements for the reduction of dioxygen by a  $\text{Mn}^{\text{II}}$  complex were observed in the presence of redox-inactive group 2 metal ions. The rate changes were correlated with an increase in the Lewis acidity of the group 2 metal ions. These studies led to the isolation of heterobimetallic complexes containing  $\text{Mn}^{\text{III}}-(\mu\text{-OH})-\text{M}^{\text{II}}$  cores ( $\text{M}^{\text{II}} = \text{Ca}^{\text{II}}, \text{Ba}^{\text{II}}$ ) in which the hydroxo oxygen atom is derived from  $\text{O}_2$ . This type of core structure has relevance to the oxygen-evolving complex within photosystem II.

Metal ions that function as Lewis acids are known to have a major influence on a variety of chemical transformations.<sup>1</sup> Often they are used in combination with redox-active transition-metal complexes to promote a variety of reactions involving the transfer of electrons.<sup>2</sup> This effect is typified in metalloproteins such as the copper–zinc superoxide dismutases, in which both metal ions have been proposed to be functionally active.<sup>3</sup> In addition, it is now widely accepted that a redox-inactive  $\text{Ca}^{\text{II}}$  ion is necessary for oxidation of water to dioxygen in the oxygen-evolving complex (OEC).<sup>4,5</sup> Examples of these effects are also found in synthetic systems: Yu showed that group 1 metal ions promote C–H bond activation in a series of  $\text{Pd}^{\text{II}}$  complexes;<sup>6</sup> Lau illustrated that Lewis acidic metal ions enhance the reactivity of metal–oxo complexes toward oxidation of alkanes;<sup>7</sup> and Collins demonstrated that secondary ions activate O-atom transfer reactions of  $\text{Mn}^{\text{V}}=\text{O}$  complexes.<sup>8</sup> Moreover, Fukuzumi and Nam recently reported that the rates of electron transfer from  $\text{Fe}^{\text{IV}}=\text{O}$  complexes are significantly altered in the presence of Lewis acidic metal ions, which led to the isolation of a complex containing an  $\text{Fe}^{\text{IV}}=\text{O}---\text{Sc}^{\text{III}}$  unit.<sup>9</sup> Fukuzumi further demonstrated that the rate of the one-electron conversion of  $\text{O}_2$  to superoxide ion is correlated with the Lewis acidities of redox-inactive metal ions,<sup>10</sup> implying that redox-inactive metal ions may play a role in the activation of dioxygen.<sup>11</sup> We report herein that the rates of  $\text{O}_2$  reduction by a monomeric  $\text{Mn}^{\text{II}}$  complex are accelerated in the presence of group 2 metal ions. These findings led to the isolation and structural characterization of a discrete heterobimetallic complex containing a  $\text{Mn}^{\text{III}}-(\mu\text{-OH})-\text{Ca}^{\text{II}}$  core,<sup>12,13</sup> a construct that is related to the active site of the OEC in photosystem II.

Our group has been investigating the influences of the secondary coordination sphere on metal-mediated processes.<sup>14</sup> In particular, we have developed ligands that promote intramolecular hydrogen-bonding (H-bonding) networks within the

secondary coordination spheres of metal ions. Most of our ligands contain H-bond donors, such as the urea-based ligand  $[\text{H}_3\text{buea}]^{3-}$ , whose inward placement of NH groups produces a positively polarized cavity (Figure 1). To reverse the polarity of the cavity, we designed the sulfonamido-based tripodal ligand  $N,N,N',N''-[2,2',2''\text{-nitrilotris(ethane-2,1-diyl)}]\text{tris}(2,4,6\text{-trimethylbenzenesulfonamido})$  ( $[\text{MST}]^{3-}$ , Figure 1)<sup>15</sup> and showed that the  $\text{SO}_2\text{R}$  groups can serve as H-bond acceptors. Previously reported ligands with sulfonamido groups are almost exclusively  $C_2$ -symmetric, such as those of Walsh,<sup>16</sup> who showed that both nitrogen and oxygen atoms are capable of coordinating to a metal ion. During the course of our studies with the  $\text{Mn}^{\text{II}}$  complex  $[\text{Mn}^{\text{II}}\text{MST}]^-$ , we discovered that the oxygen atoms of the  $\text{SO}_2\text{Ar}$  groups can bind group 2 metal ions, which appears to be a requirement for the acceleration of the dioxygen activation process.

The preparation of  $[\text{Mn}^{\text{II}}\text{MST}]^-$  was accomplished by treatment of a  $N,N$ -dimethylacetamide (DMA) solution of  $\text{H}_3\text{MST}$  with 3 equiv of NaH followed by the addition of  $\text{Mn}(\text{OAc})_2$ .<sup>17</sup> Metathesis with  $[\text{NMe}_4](\text{OAc})$  afforded  $[\text{NMe}_4][\text{Mn}^{\text{II}}\text{MST}]$  in 90% yield after workup (Scheme 1). This salt showed limited reactivity with dioxygen at 25 °C, with an initial rate of  $6.2 \times 10^{-6} \text{ s}^{-1}$  as assayed by optical spectroscopy (Figure 2). The low rate of the reaction prevented isolation of any oxidized species. However, we found that the rate of the reaction with dioxygen was accelerated in the presence of group 2 metal ions. For instance, an initial rate of  $5.8 \times 10^{-4} \text{ s}^{-1}$  was obtained when the mixture of  $[\text{NMe}_4][\text{Mn}^{\text{II}}\text{MST}]$  and dioxygen was treated with 1 equiv of  $\text{Ca}(\text{OTf})_2/15\text{-crown-5}$  (Figures 2 and 3). Addition of larger amounts of  $\text{Ca}(\text{OTf})_2/15\text{-crown-5}$  did not change this rate substantially, as only a small decrease in the initial rate was observed (Figure S1 in the Supporting Information).<sup>17</sup> The initial rate for this reaction was also affected when the  $[\text{NMe}_4][\text{Mn}^{\text{II}}\text{MST}]/\text{dioxygen}$  mixture was treated with 1 equiv of  $\text{Ba}(\text{OTf})_2/18\text{-crown-6}$ , which gave an initial rate of  $1.8 \times 10^{-5} \text{ s}^{-1}$ .<sup>18</sup> Although the role of the group 2 metal ions remains to be clarified, these results clearly indicate that the rate of  $\text{O}_2$  activation by  $[\text{Mn}^{\text{II}}\text{MST}]^-$  is dependent upon the presence of redox-inactive metal ions.

The major product of the reaction with  $\text{Ca}(\text{OTf})_2/15\text{-crown-5}$  was obtained in yields of 50–60% and exhibited a visible absorption spectrum with features at  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{M}}/\text{cm}^{-1} \text{ M}^{-1}$ ) = 450 (340), 640 (600), and 800 (sh) (Figure 3 inset) that matched the final spectrum obtained from the reaction. Analytical data

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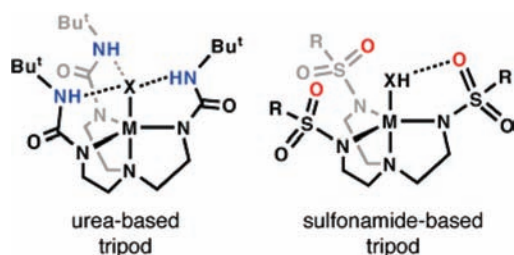


Figure 1. Examples of systems containing intramolecular H-bonds.

Scheme 1. Reactions Involving  $[\text{Mn}^{\text{II}}\text{MST}]^-$

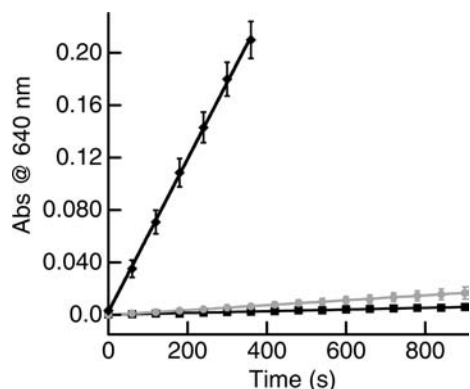
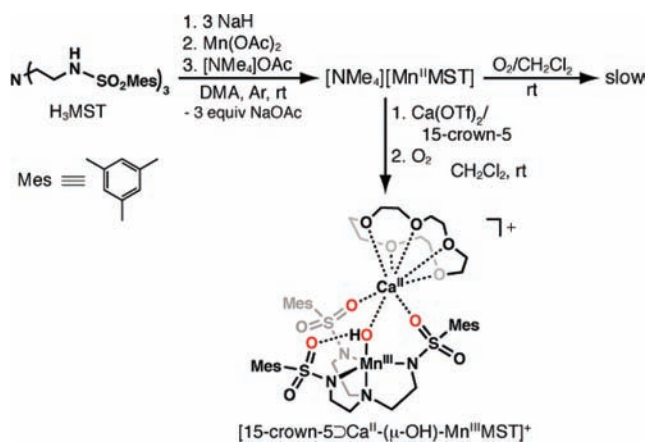


Figure 2. Initial rate data for the reaction of  $[\text{NMe}_4][\text{Mn}^{\text{II}}\text{MST}]^-$  and  $\text{O}_2$  alone (black  $\blacksquare$ ,  $6.2 \times 10^{-6} \text{ s}^{-1}$ ) and in the presence of  $\text{Ca}(\text{OTf})_2/15\text{-crown-5}$  (black  $\blacklozenge$ ,  $5.8 \times 10^{-4} \text{ s}^{-1}$ ) or  $\text{Ba}(\text{OTf})_2/18\text{-crown-6}$  (gray  $\bullet$ ,  $1.8 \times 10^{-5} \text{ s}^{-1}$ ). Reactions were performed in  $\text{CH}_2\text{Cl}_2$  at  $25^\circ\text{C}$ .

suggested a molecular formulation of  $[15\text{-crown-5} \supset \text{Ca}^{\text{II}}-(\mu\text{-OH})-\text{Mn}^{\text{III}}\text{MST}]\text{OTf}$ , which was supported by electrospray ionization mass spectrometry (ESI-MS) experiments. The ESI-MS<sup>+</sup> spectrum contained a strong ion signal at  $m/z$  1021.27 when the complex was prepared with  $^{16}\text{O}_2$ ; the mass and calculated isotopic distribution were consistent with  $[15\text{-crown-5} \supset \text{Ca}^{\text{II}}-(\mu\text{-OH})-\text{Mn}^{\text{III}}\text{MST}]^+$  (Figure S2).<sup>17</sup> When the reaction was performed under  $^{18}\text{O}_2$ , the molecular ion peak shifted by 2 mass units to  $m/z$  1023.27, indicating that the oxygen atom of the hydroxo ligand was derived from the activation of dioxygen. Moreover, our mass spectral studies indicated that

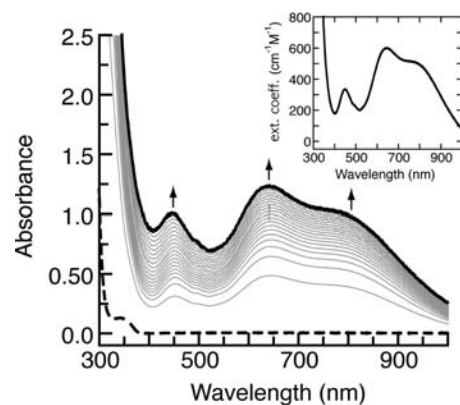


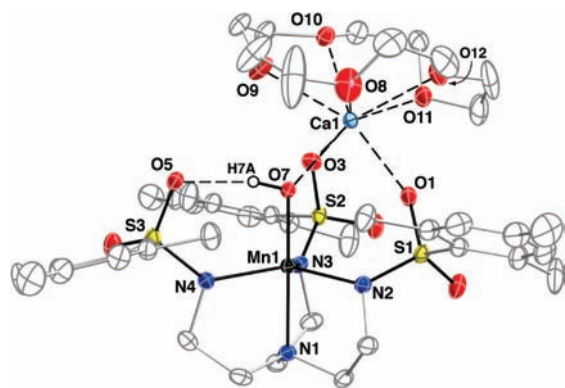
Figure 3. Electronic absorbance spectra for the reduction of dioxygen in the presence of  $[\text{Mn}^{\text{II}}\text{MST}]^-$  and  $\text{Ca}(\text{OTf})_2/15\text{-crown-5}$  in  $\text{CH}_2\text{Cl}_2$  at  $25^\circ\text{C}$ . Spectra were recorded every 30 min. The inset shows the spectrum of the isolated product,  $[15\text{-crown-5} \supset \text{Ca}^{\text{II}}-(\mu\text{-OH})-\text{Mn}^{\text{III}}\text{MST}]^+$ .

the hydroxo ligand undergoes water/hydroxo exchange reactions (Figure S3).<sup>17</sup>

The molecular structure of  $[15\text{-crown-5} \supset \text{Ca}^{\text{II}}-(\mu\text{-OH})-\text{Mn}^{\text{III}}\text{MST}]^+$  was determined by X-ray diffraction, which revealed the predicted heterobimetallic complex (Figure 4). The  $\text{Mn}^{\text{III}}$  center has an  $\text{N}_4\text{O}$  primary coordination sphere with trigonal-bipyramidal geometry. The nitrogen atoms of the  $[\text{MST}]^{3-}$  ligand coordinate to the  $\text{Mn}^{\text{III}}$  ion with a  $\text{Mn1-N1}$  bond length of  $2.075(2) \text{ \AA}$  and an average  $\text{Mn1-N}_{\text{eq}}$  bond distance of  $2.052(2) \text{ \AA}$ . The primary sphere of the  $\text{Mn}^{\text{III}}$  center is completed by a hydroxo ligand having a  $\text{Mn1-O7}$  bond distance of  $1.829(2) \text{ \AA}$  and a  $\text{N1-Mn1-O7}$  bond angle of  $176.9(1)^\circ$ . Notably, each  $\text{SO}_2\text{Ar}$  group adopts a conformation in which one of the  $\text{S=O}$  bonds is positioned nearly perpendicular to the equatorial plane, with an average  $\text{Mn-N-S-O}$  torsion angle of  $22.8(2)^\circ$ . This configuration of the  $\text{SO}_2\text{Ar}$  groups produces a cavity that forms an intramolecular H-bond between the  $\text{Mn}^{\text{III}}-\text{OH}$  unit and  $\text{O5}$  of the  $[\text{MST}]^{3-}$  ligand [ $\text{O7} \cdots \text{O5}$  distance =  $2.693(2) \text{ \AA}$ ].<sup>19</sup>

The most striking feature of the structure is the placement of a  $\text{Ca}^{\text{II}}$  ion within the secondary coordination sphere of the  $\text{Mn}^{\text{III}}$  center. The  $\text{Ca}^{\text{II}}$  ion interacts with the complex through  $\text{O7}$  of the  $\text{Mn}^{\text{III}}-\text{OH}$  unit and  $\text{O1}$  and  $\text{O3}$  from two of the sulfonamide groups of the  $[\text{MST}]^{3-}$  ligand; it appears that these oxygen atoms are positioned in such a way that they form an auxiliary face-capping site for the binding of additional metal ions. The  $\text{O7}$  atom of the hydroxo ligand bridges the two metal centers with a  $\text{Mn1-O7-Ca1}$  bond angle of  $127.49(9)^\circ$  and a  $\text{Ca}^{\text{II}} \cdots \text{Mn}^{\text{III}}$  separation of  $3.748(2) \text{ \AA}$ . The  $\text{Ca1} \cdots \text{O7}$  bond distance is  $2.342(2) \text{ \AA}$ , which is similar to the  $\text{Ca1} \cdots \text{O1}$  and  $\text{Ca1} \cdots \text{O3}$  bond lengths of  $2.333(2)$  and  $2.370(2) \text{ \AA}$ . The five oxygen atoms of the crown ether fill the remaining coordination sites on  $\text{Ca1}$ , and the average  $\text{Ca1} \cdots \text{O}_{15\text{-crown-5}}$  distance is  $2.48 \text{ \AA}$ . Also, the  $15\text{-crown-5}$  ligand adopts an "inverted umbrella" structure, whereby the  $\text{Ca}^{\text{II}}$  ion is displaced out of the crown ether toward the  $[\text{MST}]^{3-}$  ligand.<sup>20</sup>

To our knowledge,  $[15\text{-crown-5} \supset \text{Ca}^{\text{II}}-(\mu\text{-OH})-\text{Mn}^{\text{III}}\text{MST}]^+$  represents the first example of a structurally characterized species containing a  $\text{Mn}^{\text{III}}-(\mu\text{-OH})-\text{Ca}^{\text{II}}$  core. In fact, discrete  $\text{Ca}^{\text{II}}-\text{OH}$  systems are rare, with the  $\text{LCa}^{\text{II}}-(\mu\text{-OH})_2-\text{Ca}^{\text{II}}\text{L}$  homodimer of Roesky the only other structurally characterized complex.<sup>21</sup> In that complex, each calcium center is five-coordinate, and the  $\text{Ca}-\text{O}(\text{H})$  distances ( $<2.25 \text{ \AA}$ ) are significantly shorter



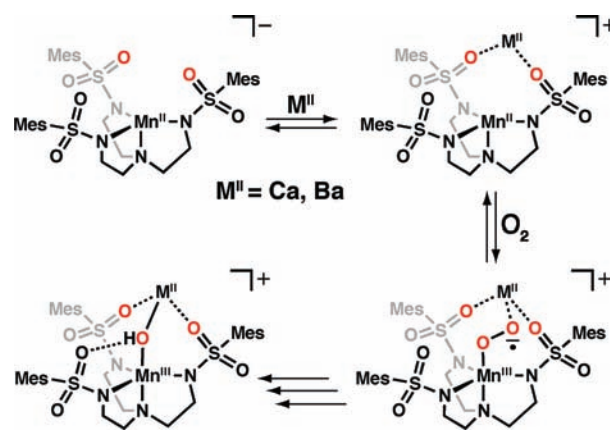
**Figure 4.** Thermal ellipsoid diagram depicting the molecular structure of  $[15\text{-crown-}5\text{Ca}^{\text{II}}-(\mu\text{-OH})\text{-Mn}^{\text{III}}\text{MST}]^+$ . Ellipsoids are drawn at the 50% probability level, and for clarity, only the hydroxo hydrogen atom has been shown. Selected bond lengths (Å) and angles (deg): Mn1–O7, 1.829(2); Mn1–N1, 2.075(2); Mn1–N2, 2.019(2); Mn1–N3, 2.107(2); Mn1–N4, 2.029(2); Mn1...Ca1, 3.7478(6); Ca1–O1, 2.332(2); Ca1–O3, 2.369(2); Ca1–O7, 2.342(2); Ca1–O8, 2.490(3); Ca1–O9, 2.508(2); Ca1–O10, 2.492(2); Ca1–O11, 2.486(2); Ca1–O12, 2.453(2); O7–Mn1–N2, 96.95(8); O7–Mn1–N4, 96.58(8); N2–Mn1–N4, 131.81(10); O7–Mn1–N1, 176.94(9); N2–Mn1–N1, 81.83(9); N4–Mn1–N1, 82.25(9); O7–Mn1–N3, 101.09(8); N2–Mn1–N3, 109.38(9); N4–Mn1–N3, 112.93(9); N1–Mn1–N3, 81.97(9); Mn1–O7–Ca1, 127.49(9).

than those observed in  $[15\text{-crown-}5\text{Ca}^{\text{II}}-(\mu\text{-OH})\text{-Mn}^{\text{III}}\text{MST}]^+$ . We are also aware of only three other structurally characterized molecular systems containing calcium/manganese bridged units: the  $\text{Mn}_{13}\text{Ca}_2$  cluster prepared by Christou,<sup>22a</sup> the  $\text{Mn}_4\text{Ca}$  system of Powell,<sup>22b</sup> and the  $\text{Mn}_3\text{CaNa}$  cluster of Reedijk.<sup>22c</sup>

Studies of the properties of heterometallic complexes with manganese/calcium cores have been sparked by the OEC of photosystem II. Sufficient information is available to show that the active site of the OEC contains a  $\text{Mn}_4\text{Ca}$  cluster that is surrounded by a network of H-bonds. Most current mechanistic proposals stipulate that the calcium center has a direct role in water oxidation,<sup>4c,5</sup> a premise that is supported by a recent X-ray structure of the OEC at a resolution of 1.9 Å.<sup>4f</sup> This structure shows that the  $\text{Ca}^{\text{II}}$  ion has two bound water molecules and is connected to the manganese centers through oxygen-containing bridging ligands, some of which could possibly be oriented in a manner similar to that found in  $[15\text{-crown-}5\text{Ca}^{\text{II}}-(\mu\text{-OH})\text{-Mn}^{\text{III}}\text{MST}]^+$ . Moreover, the isolation of  $[15\text{-crown-}5\text{Ca}^{\text{II}}-(\mu\text{-OH})\text{-Mn}^{\text{III}}\text{MST}]^+$  indicates that inclusion of sulfonamido groups into ligands may provide a new synthetic method for the preparation of these types of heterometallic complexes.

We have presented data showing that group 2 metal ions have a marked influence on the rate of dioxygen activation by a monomeric  $\text{Mn}^{\text{II}}$  complex. Our findings showed an increase in the initial rate in the presence of  $\text{Ca}^{\text{II}}$  and  $\text{Ba}^{\text{II}}$  ions, with the reaction in the presence of  $\text{Ca}^{\text{II}}$  ions being faster by a factor of 35. These results complement those reported by Fukuzumi,<sup>10a</sup> who showed that the rate of electron transfer from  $[\text{Co}^{\text{II}}(\text{tetraphenylporphyrin})]$  to  $\text{O}_2$  is also accelerated in the presence of  $\text{Ca}^{\text{II}}$  and  $\text{Ba}^{\text{II}}$  ions; in this one-electron transfer process,  $\text{Ca}^{\text{II}}$  ions increased the rate by a factor of 22 relative to  $\text{Ba}^{\text{II}}$  ions. The similarity of those rate data to the data for our systems offers a possible explanation of why dioxygen activation with  $[\text{Mn}^{\text{II}}\text{MST}]^-$  depends on the presence of group 2 ions (Scheme 2). The reduction of dioxygen to superoxide could be dependent on the prior formation of a

**Scheme 2.** Proposed Role of the Redox-Inactive Metal Ions in the Activation of Dioxygen



heterometallic  $\text{Mn}^{\text{II}}\text{Ca}^{\text{II}}$  complex that coordinates dioxygen and then facilitates electron transfer to form a putative superoxo adduct. The rate of intramolecular electron transfer to generate a putative  $\text{Mn}^{\text{III}}(\text{superoxo})\text{-M}^{\text{II}}$  species would depend on the Lewis acidity of the group 2 metal ion, which would help alleviate the buildup of negative charge. This possible function of the redox-inactive metal ion is reminiscent of the role played by the H-bonding cavities in the metal complexes of our urea-based tripods (Figure 1). In these systems, the positively polarized cavities promote the binding and activation of dioxygen through the formation of intramolecular H-bonds.<sup>14,23</sup> The results found with  $[\text{Mn}^{\text{II}}\text{MST}]^-$  illustrate the possibility that redox-inactive metal ions can also be used to facilitate the activation of dioxygen, which in turn may provide another way to control and enhance the reactivity of transition-metal complexes.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Experimental details, supporting tables and figures, and crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) Experimental details can be found in the Supporting Information.

(18) The molecular structure of the reaction product was determined by X-ray diffraction methods to be  $[18\text{-crown-6}\supset\text{Ba}^{\text{II}}-(\mu\text{-OH})-\text{Mn}^{\text{III}}\text{MST}]^+$ , which is similar to  $[15\text{-crown-5}\supset\text{Ca}^{\text{II}}-(\mu\text{-OH})-\text{Mn}^{\text{III}}\text{MST}]^+$ .<sup>17</sup>

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