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Dioxygen activation by a novel manganese(II) thiolate complex with hydrotris(3,5-diisopropylpyrazol-1-yl)borate ligand

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Reaction of a $\mathrm{Mn^{II}}$ thiolate complex bearing hydrotris(3,5-diisopropylpyrazol-1-yl)borate with O_2 resulted in O–O bond activation to give a dinuclear $\mathrm{Mn^{III}}$ bis(μ-oxo) complex and a ligand-oxygenated dinuclear $\mathrm{Mn^{III}}$ μ-oxo complex, or the dinuclear $\mathrm{Mn^{III,IV}}$ μ-acetato-bis(μ-oxo) complex in the presence of a $\mathrm{Mn^{II}}$ acetate complex.

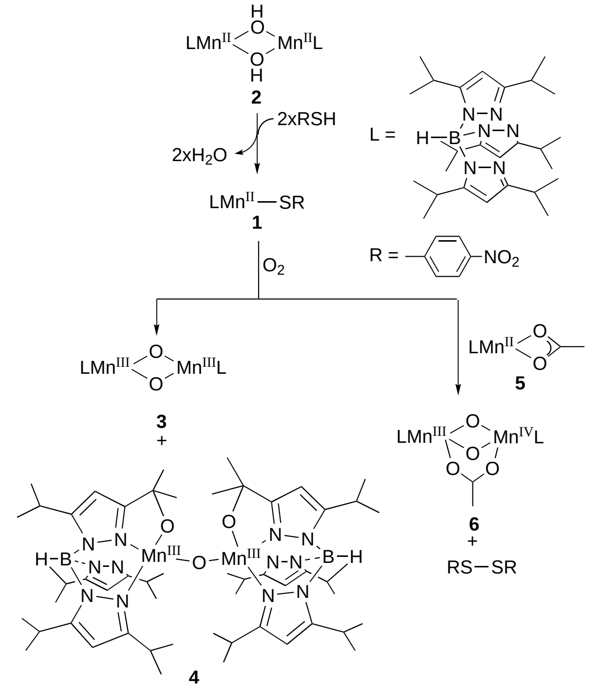
Dioxygen activation on transition-metal ions is one of the attractive topics from the standpoints of bioinorganic and synthetic chemistry. Manganese–oxygen (O_2^{-}, O_2^{2-}, O^{2-}, *etc.*) species are suggested to take part in the physiological dioxygen metabolism and catalytic oxidation of organic compounds.[1] By using the hindered tris(pyrazolyl)borate ligand, hydrotris(3,5-diisopropylpyrazol-1-yl)borate (L), we have investigated the chemistry of Mn complexes with dioxygen and its derivatives, for example, synthesis and characterization of the mononuclear $\mathrm{Mn^{III}}$ peroxo complex,[2] aliphatic C–H bond oxygenation in the dimanganese complex with O_2,[3] and superoxide anion dismutation by the $\mathrm{Mn^{II}}$–carboxylate complexes.[4] It is notable that the co-ordinatively unsaturated carboxylate complex, $\mathrm{Mn^{II}L(O_2CPh)}$,[4,5] cannot activate O_2, although the $\mathrm{Fe^{II}}$ derivative shows reversible O_2 binding ability to give the corresponding dinuclear $\mathrm{Fe^{III}}$–μ-peroxo complex.[6] In order to realize O_2 activation on a MnL complex, we adopted a thiolate ligand, which is known to be a highly electron-donating soft base compared to such ligands as carboxylate, so as to increase the electron density at metal centers. In this communication, we report the dioxygen activation by a co-ordinatively unsaturated $\mathrm{Mn^{II}L}$–thiolate complex, and the intermediacy of a Mn–O_2 adduct has been confirmed by a trapping experiment.

Synthesis of the thiolate complex and its oxygenation reactions are summarized in Scheme 1. The $\mathrm{Mn^{II}}$ thiolate complex $\mathrm{Mn^{II}L(SC_6H_4NO_2\text{-}}$*p*$)$ **1** † was prepared by reaction of a dinuclear $\mathrm{Mn^{II}}$ bis(μ-hydroxo) complex, LMn(μ-OH)$_2$MnL **2**,[7] with *p*-nitrobenzenethiol under Ar. Formulation of complex **1** is based on its IR spectrum, with sharp absorptions around 1590–1570 cm^{-1} arising from the *p*-nitrophenyl group, and its field desorption MS spectrum [*m*/*z* = 675 (*M*$^+$)]. The Mn center of **1** is assumed to have a co-ordinatively unsaturated geometry as found in the analogous PhO- and RS-$\mathrm{LFe^{II}}$ complexes.[8]

As expected, the thiolate complex **1** readily reacted with dioxygen in a manner similar to the dinuclear $\mathrm{Mn^{II}}$ bis(μ-hydroxo) complex **2**.[3] When a toluene solution of **1** was stirred under O_2 atmosphere for 1 d, the solution changed from yellow to dark brown. From this dark brown solution, three products were isolated: the dinuclear $\mathrm{Mn^{III}}$ bis(μ-oxo) complex, LMn(μ-O)$_2$MnL **3**,[7] the ligand-oxygenated dinuclear $\mathrm{Mn^{III}}$ complex **4**,[3] and the corresponding disulfide ($\mathrm{O_2NC_6H_4S{-}SC_6H_4NO_2}$).‡ The thiolate complex **1** was not hydrolyzed by treatment with an excess amount of H_2O [equation (1)]. We can

$$\underset{\mathbf{1}}{\mathrm{LMn^{II}{-}SR}} + \mathrm{H_2O} \not\longrightarrow \mathbf{2} + \mathrm{RSH} \quad (1)$$

conclude that the present oxidation reactions proceed *via* degradation of Mn–O_2 species which are formed by reaction of O_2 and **1** (not **2**) as will be discussed below.



Scheme 1

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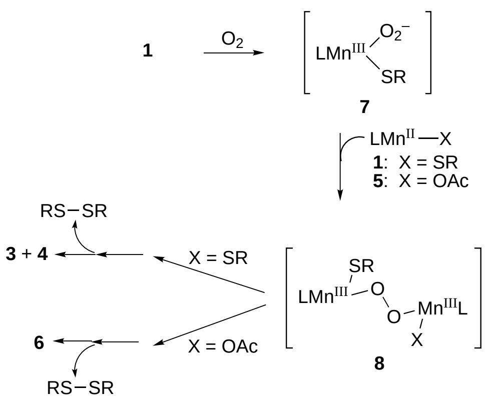
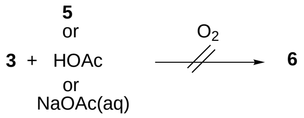
† Spectroscopic data for complex **1** (Found: C, 59.13; H, 7.40; N, 14.45. Calc. for $\mathrm{C_{33}H_{50}BMnN_7O_2}$: C, 58.75; H, 7.47; N, 14.53%). IR (KBr pellet, $\tilde{\nu}/cm^{-1}$): 2550m (BH), 1586, 1571s (PhC=C and NO_2). Field desorption MS: *m*/*z* 675 (*M*$^+$). The two co-ordinating MeCN molecules are dissociated from the metal center in a non-co-ordinating solvent such as toluene or CH_2Cl_2, evidenced by the reversible color change from yellow (in toluene) to reddish orange (in MeCN). UV/VIS data: [toluene solution, 23 °C, nm ($\varepsilon/\mathrm{M^{-1}\,cm^{-1}}$)] 322 (9860); [MeCN solution, 23 °C, nm ($\varepsilon/\mathrm{M^{-1}\,cm^{-1}}$)] 318 (7580), 487 (9740). In the present study, oxygenation reactions were carried out in toluene to avoid the co-ordination of solvent. The monomeric structure of **1** has been confirmed by X-ray crystallography. Single crystals suitable for analysis have been obtained from MeCN solution. The $\mathrm{Mn^{II}}$ center is co-ordinated by an N_5S donor set including two MeCN molecules. Crystal data for $\mathrm{MnL(SC_6H_4NO_2)(MeCN)_2\cdot 3.5MeCN}$: $\mathrm{C_{44}H_{68}BMnN_{12.5}O_2S}$, $M = 901.9$, monoclinic, space group *C*2/*c* (no. 15), $a = 42.99(6)$, $b = 12.475(4)$, $c = 19.686(6)$ Å, $\beta = 94.85(6)°$, $U = 10\,519(5)$ Å^3, $Z = 8$, $T = -60$ °C, $D_c = 1.14$ g cm^{-1}, μ(Mo-Kα) = 3.36 cm^{-1}, R (R') = 10.01 (10.98)% for 3728 reflections with 484 parameters. CCDC reference number 186/859.

‡ The disulfide product was obtained almost quantitatively. The yield (based on complex **1**) was determined by GC analysis. Yield of RS–SR in the reaction of **1** with O_2 in the absence of **5** 88.2%, in the presence of **5** 87.4%.



Scheme 2

Although no Mn–O_2 species was detected, its participation was supported by the following trapping experiment. Reaction of **1** with dioxygen in the presence of a Mn^{II} acetate complex, MnL(OAc) **5**,§ resulted in the predominant formation of the $Mn^{III,IV}$ μ-acetato-bis(μ-oxo) complex, LMn(μ-OAc)(μ-O)$_2$-MnL **6**¶ (59% isolated yield based on **1**),[9] and the disulfide.‡ It is worth noting that the acetate complex **5** is sluggish toward oxidation under similar reaction conditions. When a toluene solution of **5** was stirred under O_2, the solution turned from pale yellow to pale brown, but the reaction was very slow (over a week), and neither the Mn–O_2 adducts nor the $Mn^{III,IV}$ complex **6** were detected. In addition, reactions of the bis(μ-oxo) complex **3** and the acetate complex **5** or aqueous NaOAc or acetic acid under O_2 did not yield **6** [equation (2)]. Therefore, it is concluded that the dinuclear $Mn^{III,IV}$ complex **6** is formed *via* a trapping process of the Mn–O_2 adduct by **5**.



$$\mathbf{3} + \begin{matrix}\mathbf{5}\\ \text{or}\\ \text{HOAc}\\ \text{or}\\ \text{NaOAc(aq)}\end{matrix} \xrightarrow[]{O_2} \mathbf{6} \quad (2)$$

Plausible mechanisms for the present O_2 activation reactions are summarized in Scheme 2. Reaction of complex **1** with O_2 may form a Mn^{III}–superoxo complex **7**, which further reacts with another molecule of the Mn^{II} complex **1** or **5** to give the corresponding dinuclear Mn^{III} μ-peroxo intermediate **8**. Metal–superoxo species are known to work as nucleophiles, therefore, the nucleophilic attack of anionic **7** at the positive Mn^{II} center of **5** is more favorable than that of **1** and therefore the trapping experiment is successful. Subsequent homolysis of the O–O and Mn–S bonds|| results in the formation of **3**, **4** and/or **6**.[10] During the formation of the μ-acetato-bis(μ-oxo) complex **6**, the acetate ligand in **5** bridges the two metal centers (so-called 'carboxylate shift') as observed in the formation of the dinuclear Fe^{III} μ-peroxo complex containing L.[11]

It is known that reduction of dioxygen to superoxide in a one-electron transfer step has a more negative electrochemical potential than that of the two-electron reduction (O_2 to O_2^{2-}).[12] The O_2 activation ability of the co-ordinatively unsaturated thiolate complex **1** may arise from the high electron density at the Mn^{II} center as we anticipated. Thiolate complexes with redox-active metal ions are known to cause homolytic metal–sulfur bond cleavage to give the corresponding disulfides and reduced metal ions, in fact, the thiolate ligand of **1** works as a good leaving group as well as a reductant toward the Mn center. In the case of our previous O_2 activation studies by the hydroxo complex **2**,[3] the dinuclear structure constructed by two five-co-ordinated Mn^{II} centers is advantageous for the two-electron reduction of O_2 giving the μ-peroxo intermediates, and the hydroxide ligands are proposed to be eliminated as H_2O during further O–O bond activation.[3] Therefore, it is concluded that a requisite of the O_2-activating Mn^{II} complex is the presence of co-ordinatively unsaturated metal centers with O_2 reducing potential, and good leaving ligands to induce further O–O bond activation.

In conclusion, O_2 activation has been achieved by a Mn^{II}–thiolate complex and the resulting superoxo intermediate reacts with an acetate complex to give a μ-peroxo intermediate **8**, which is converted into the μ-acetato-bis(μ-oxo) complex **6** after O–O and Mn–S bond rupture. Further investigations including detection of the O_2 adducts and oxidation reactions of external substrates will be performed.

Acknowledgements

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§ The acetate complex **5** was obtained by treating $Mn(OAc)_2\cdot 4H_2O$ with KL. Spectroscopic data for **5** (Found: C, 59.84; H, 8.65; N, 14.61. Calc. for $C_{29}H_{49}BMnN_6O_2$: C, 60.11; H, 8.52; N, 14.50%). IR (KBr pellet, $\tilde{\nu}$/cm^{-1}): 2545m (BH), 1561s [$CO_{2(asym)}$]. Field desorption MS: *m*/*z* 579 (M^+). The acetate ligand is assumed to bind to the Mn^{II} center in a bidentate fashion on the basis of the similarity of the $\nu[CO_{2(asym)}]$ of the benzoate analogue $MnL(O_2CPh)$ (1568 cm^{-1}), which has a five-co-ordinated distorted trigonal bipyramid Mn^{II} center with the bidentate carboxylate ligand established by crystallography (see refs. 4 and 5). The $\nu[CO_{2(asym)}]$ of **5** is indistinguishable from other peaks arising from the MnL moiety, whereas the unidentate acetatozinc complex with the same ligand gives $\nu[CO_{2(asym)}]$ and $\nu[CO_{2(asym)}]$ at 1601 and 1331 cm^{-1}, respectively.

¶ The dinuclear $Mn^{III,IV}$ μ-acetato-bis(μ-oxo) complex **6** was identified by comparison with the data (EPR, field desorption MS, IR and X-ray crystallography) of an authentic sample (see ref. 9).

|| The O–O bond homolysis of a dinuclear μ-peroxo core $[M^{n+}(\mu\text{-}O_2^{2-})M^{n+}]$ gives the corresponding two-electron oxidized bis(μ-oxo) core $[M^{(n+1)+}(\mu\text{-}O^{2-})_2M^{(n+1)+}]$ and metal–sulfur bond homolysis of a $M^{n+}(SR)$ core yields a one-electron reduced metal $[M^{(n-1)+}]$ center.