

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

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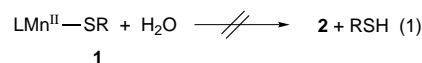
Reaction of a Mn^{II} thiolate complex bearing hydrotris(3,5-diisopropylpyrazol-1-yl)borate with O₂ resulted in O–O bond activation to give a dinuclear Mn^{III} bis(μ-oxo) complex and a ligand-oxygenated dinuclear Mn^{III} μ-oxo complex, or the dinuclear Mn^{III,IV} μ-acetato-bis(μ-oxo) complex in the presence of a 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 (O₂⁻, O₂²⁻, O²⁻, 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 Mn^{III} peroxo complex,² aliphatic C–H bond oxygenation in the dimanganese complex with O₂,³ and superoxide anion dismutation by the Mn^{II}–carboxylate complexes.⁴ It is notable that the co-ordinatively unsaturated carboxylate complex, Mn^{II}L(O₂CPh),^{4,5} cannot activate O₂, although the Fe^{II} derivative shows reversible O₂ binding ability to give the corresponding dinuclear Fe^{III}–μ-peroxo complex.⁶ In order to realize O₂ 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 Mn^{II}L–thiolate complex, and the intermediacy of a Mn–O₂ adduct has been confirmed by a trapping experiment.

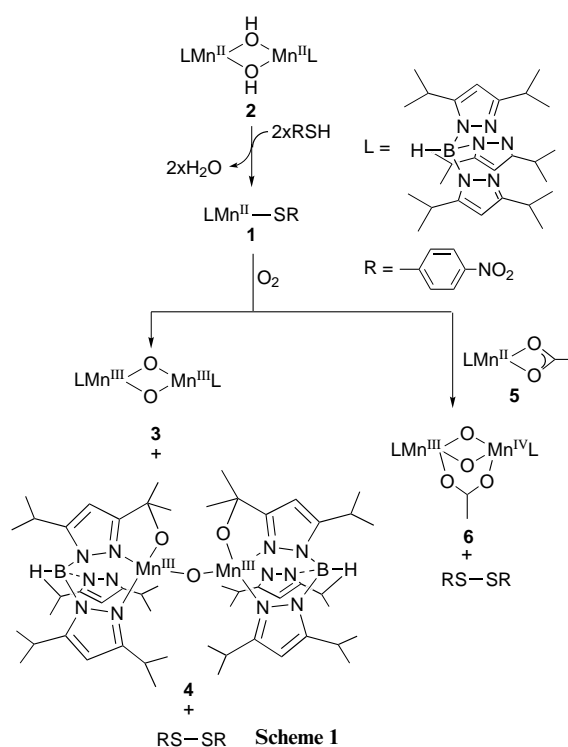
Synthesis of the thiolate complex and its oxygenation reactions are summarized in Scheme 1. The Mn^{II} thiolate complex Mn^{II}L(SC₆H₄NO₂-*p*) **1** † was prepared by reaction of a dinuclear Mn^{II} bis(μ-hydroxo) complex, LMn(μ-OH)₂MnL **2**,⁷ with *p*-nitrobenzenethiol under Ar. Formulation of complex **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-LFe^{II} complexes.⁸

As expected, the thiolate complex **1** readily reacted with dioxygen in a manner similar to the dinuclear Mn^{II} bis(μ-hydroxo) complex **2**.³ When a toluene solution of **1** was stirred under O₂ atmosphere for 1 d, the solution changed from yellow to dark brown. From this dark brown solution, three products were isolated: the dinuclear Mn^{III} bis(μ-oxo) complex, LMn(μ-O)₂MnL **3**,⁷ the ligand-oxygenated dinuclear Mn^{III} complex **4**,³ and the corresponding disulfide (O₂NC₆H₄S–SC₆H₄NO₂). ‡ The thiolate complex **1** was not hydrolyzed by treatment with an excess amount of H₂O [equation (1)]. We can

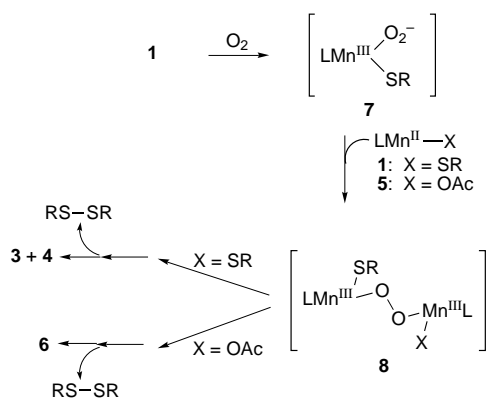


conclude that the present oxidation reactions proceed *via* degradation of Mn–O₂ species which are formed by reaction of O₂ and **1** (not **2**) as will be discussed below.



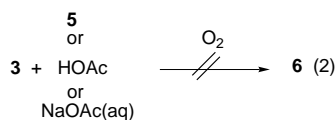
† Spectroscopic data for complex **1** (Found: C, 59.13; H, 7.40; N, 14.45. Calc. for C₃₃H₅₀BMnN₇O₂: C, 58.75; H, 7.47; N, 14.53%). IR (KBr pellet, $\tilde{\nu}/\text{cm}^{-1}$): 2550m (BH), 1586, 1571s (PhC=C and NO₂). Field desorption MS: *m/z* 675 (*M*⁺). The two co-ordinating MeCN molecules are dissociated from the metal center in a non-co-ordinating solvent such as toluene or CH₂Cl₂, evidenced by the reversible color change from yellow (in toluene) to reddish orange (in MeCN). UV/VIS data: [toluene solution, 23 °C, nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)] 322 (9860); [MeCN solution, 23 °C, nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)] 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 Mn^{II} center is co-ordinated by an N₃S donor set including two MeCN molecules. Crystal data for MnL(SC₆H₄NO₂)(MeCN)₂·3.5MeCN: C₄₄H₆₈BMnN_{12.5}O_{2.5}S, *M* = 901.9, monoclinic, space group C2/c (no. 15), *a* = 42.99(6), *b* = 12.475(4), *c* = 19.686(6) Å, β = 94.85(6)°, *U* = 10 519(5) Å³, *Z* = 8, *T* = -60 °C, *D_c* = 1.14 g cm⁻³, $\mu(\text{Mo-K}\alpha)$ = 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 O₂ in the absence of **5** 88.2%, in the presence of **5** 87.4%.



Scheme 2

Although no Mn–O₂ 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 O₂, the solution turned from pale yellow to pale brown, but the reaction was very slow (over a week), and neither the Mn–O₂ 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 O₂ 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–O₂ adduct by **5**.

Plausible mechanisms for the present O₂ activation reactions are summarized in Scheme 2. Reaction of complex **1** with O₂ 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-

§ The acetate complex **5** was obtained by treating Mn(OAc)₂·4H₂O with KL. Spectroscopic data for **5** (Found: C, 59.84; H, 8.65; N, 14.61. Calc. for C₂₉H₄₉BMnN₆O₂: C, 60.11; H, 8.52; N, 14.50%). IR (KBr pellet, $\tilde{\nu}/\text{cm}^{-1}$): 2545m (BH), 1561s [CO_{2(assym)}]. 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 $\nu[\text{CO}_{2(assym)}]$ of the benzoate analogue MnL(O₂CPh) (1568 cm⁻¹), which has a five-co-ordinated distorted trigonal bipyramidal Mn^{II} center with the bidentate carboxylate ligand established by crystallography (see refs. 4 and 5). The $\nu[\text{CO}_{2(assym)}]$ of **5** is indistinguishable from other peaks arising from the MnL moiety, whereas the unidentate acetatozinc complex with the same ligand gives $\nu[\text{CO}_{2(assym)}]$ and $\nu[\text{CO}_{2(assym)}]$ 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 [Mⁿ⁺(μ -O₂²⁻)Mⁿ⁺] gives the corresponding two-electron oxidized bis(μ -oxo) core [M⁽ⁿ⁺¹⁾⁺(μ -O²⁻)₂M⁽ⁿ⁺¹⁾⁺] and metal–sulfur bond homolysis of a Mⁿ⁺(SR) core yields a one-electron reduced metal [M⁽ⁿ⁻¹⁾⁺] center.

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 (O₂ to O₂²⁻).¹² The O₂ 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 O₂ 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 O₂ giving the μ -peroxo intermediates, and the hydroxide ligands are proposed to be eliminated as H₂O during further O–O bond activation.³ Therefore, it is concluded that a requisite of the O₂-activating Mn^{II} complex is the presence of co-ordinatively unsaturated metal centers with O₂ reducing potential, and good leaving ligands to induce further O–O bond activation.

In conclusion, O₂ 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 O₂ adducts and oxidation reactions of external substrates will be performed.

Acknowledgements

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