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The First Synthesis and Structural Characterization of Alkylperoxo Complex of Manganese(II)

Hidehito Komatsuzaki,[†,‡] Naoko Sakamoto,[‡] Minoru Satoh,[‡] Shiro Hikichi,*[,†] Munetaka Akita,[†] and Yoshihiko Moro-oka*[,†]

Research Laboratory of Resources Utilization, Tokyo Institute of Technology 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan, and Department of Chemistry and Material Engineering, Ibaraki National College of Technology, 866 Nakane, Hitachinaka 312-8508, Japan

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Transition metal−alkylperoxo (M−OO−alkyl) complexes are suggested to play an important role in oxygenation reactions effected by transition metal catalysts.[1,2] They are also considered as analogues of a metal−hydroperoxo (M−OO−H) species, which is widely accepted as a key intermediate in biological dioxygen metabolism.[3] To elucidate the mechanism of oxidation reactions involving M−OOR (R = alkyl, H), structure and reactivity of transition metal complexes with alkylperoxides have attracted increasing attention. However, only a limited number of transition metal−alkylperoxo complexes have been isolated and characterized, since low-valent metal−alkylperoxo complexes are generally unstable due to their high susceptibility to the metal center oxidation.[4−6] In fact, upon treatment with an alkyl hydroperoxide, some Mn compounds induce oxygenation of hydrocarbons[7] or yield a higher valent metal-oxo complex,[8,12b] but no alkylperoxo complexes of them have been detected so far.[9] Manganese−oxygen species have attracted much attention because they take part in the physiological dioxygen metabolism [10] and the synthetic oxidation reactions.[11−13] In this communication, we report the first isolation and X-ray structure determination of an alkylperoxo complex of Mn(II) with the hindered hydrotris(pyrazolyl)borate ligand.[14]

Previously we reported that reaction of the divalent metal−hydroxo complex $[\mathrm{Tp}^{\mathrm{Pr}^i{}_2}\mathrm{M}^{\mathrm{II}}(\mathrm{OH})]_2$ ($\mathrm{Tp}^{\mathrm{Pr}^i{}_2}$ = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate) with alkyl hydroperoxide led to the successful isolation and characterization of the corresponding alkylperoxo complexes, $\mathrm{Tp}^{\mathrm{Pr}^i{}_2}\mathrm{M}^{\mathrm{II}}(\mathrm{OOR})$ (M = Co and Cu, R = Bu^t and $\mathrm{CMe_2Ph}$).[4a,b] But application of this method to the Mn system resulted in oxidation of the Mn(II)−hydroxo complex to give the dinuclear Mn(III)−bis(μ-oxo) complex, $[\mathrm{Tp}^{\mathrm{Pr}^i{}_2}\mathrm{Mn}^{\mathrm{III}}(\mu\text{-}\mathrm{O})]_2$, [15] and the desired alkylperoxo species could not be detected even at −78 °C. Then we attempted isolation of the alkylperoxo species by using the sterically more hindered ligand $\mathrm{Tp}^{\mathrm{Bu}^t,\mathrm{Pr}^i}$ (=hydrotris(3-*tert*-butyl-5-*iso*-propyl-1-pyrazolyl)borate).[4b]

The $\mathrm{Tp}^{\mathrm{Bu}^t,\mathrm{Pr}^i}$ derivative of a hydroxo complex, $\mathrm{Tp}^{\mathrm{Bu}^t,\mathrm{Pr}^i}\mathrm{Mn}^{\mathrm{II}}(\mathrm{OH})$ (**2**), which was prepared by hydrolysis of the corresponding

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[†] Tokyo Institute of Technology.

[‡] Ibaraki National College of Technology.

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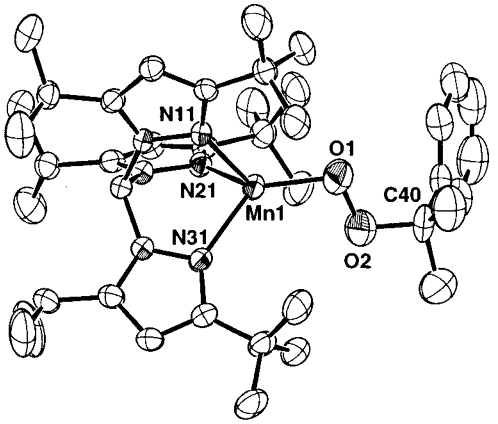
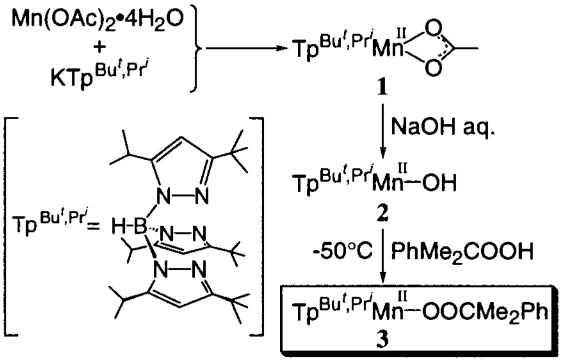


Figure 1. Crystal structure of **3**·MeCN (drawn at the 50% probability level). All hydrogen atoms and the MeCN molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Mn−O1, 1.964 (3); Mn−N11, 2.132 (3); Mn−N21, 2.161 (3); Mn−N31, 2.159 (3); O1−O2, 1.411 (4); O2−C40, 1.463 (4); O1−Mn−N11, 118.4 (1); O1−Mn−N21, 124.8 (1); O1−Mn−N31, 130.8 (1); N11−Mn−N21, 89.14 (10); N11−Mn−N31, 88.96 (10); N21−Mn−N31, 92.99 (10); Mn−O1−O2, 105.1 (2); O1−O2−C40, 109.2 (3).

Scheme 1



acetato complex **1** with aqueous NaOH solution, reacted with an equimolar amount of cumyl hydroperoxide at −50 °C to yield a corresponding Mn(II)−cumylperoxo complex, $\mathrm{Tp}^{\mathrm{Bu}^t,\mathrm{Pr}^i}\mathrm{Mn}^{\mathrm{II}}$(O-OCMe$_2$Ph) (**3**), in 43% isolated yield (Scheme 1).[16] Single crystals of **3** suitable for X-ray analysis were obtained by recrystallization from a MeCN/Et$_2$O solution at −20 °C. As shown in Figure 1, the geometry of the manganese ion in **3** was best described as a slightly distorted tetrahedron coordinated by the oxygen atom of the end-on (η^1) binding alkylperoxide ligand and the three pyrazolyl nitrogen atoms. The smallest M−O−O bending angle of **3** (105.1(2)°) in all of those observed for the transition metal-η^1-alkylperoxo complexes and relatively short Mn−O2 distance (2.700(3) Å) may imply the contribution of weak π-bonding interaction of the alkylperoxide to the Mn center, but the η^2 (= side-on)-alkylperoxo complexes are known only for the electron-deficient d^0 metal complexes (Ti$^{\mathrm{IV}}$ and V$^{\mathrm{V}}$) so far.[5i,k] The O−O bond length of 1.411(4) Å is in the range of the O−O lengths previously reported for alkylperoxo−transition metal complexes.[4,5] The valence of the manganese ion was identified to be +2 on the basis of the lack of a counteranion in the unit cell. EPR-active and colorless properties of **3** also supports the oxidation state of the Mn centers in **3** is +2.[17] For Fe$^{\mathrm{III}}$−OOR species, intense LMCT bands are observed around 500−650 nm, [6] but Mn$^{\mathrm{II}}$ complex **3** exhibits very weak absorption in the visible light region (484 nm (sh, $\epsilon = 40$ M^{-1} cm^{-1})), though number of d-electrons of Fe(III) and Mn(II) is same (= d^5). As mentioned above, the attempts to isolate the Mn(II) alkylperoxo complex with the less hindered $\mathrm{Tp}^{\mathrm{Pr}^i_2}$ ligand were unsuccessful. Because the electron-donating ability of $\mathrm{Tp}^{\mathrm{Bu}^t,\mathrm{Pr}^i}$ to the metal center may be comparable to that of $\mathrm{Tp}^{\mathrm{Pr}^i_2}$,[14] the successful isolation of the low-valent Mn(II)−alkylperoxo complex **3** may result from the highly sterically demanding property of the $\mathrm{Tp}^{\mathrm{Bu}^t,\mathrm{Pr}^i}$ ligand. To date, four structures of peroxo (O$_2^{2-}$) complexes of Mn(III) and/or Mn(IV), including $\mathrm{Tp}^{\mathrm{Pr}^i_2}\mathrm{Mn}^{\mathrm{III}}(\eta^2\text{-O}_2)(3,5\text{-Pr}^i_2\mathrm{pzH})$ prepared by us, have been characterized by X-ray crystallography, [18] but no Mn(II)−peroxo (O$_2^-$, O$_2^{2-}$, OOH$^-$, OOR$^-$, and OOC(O)R$^-$) complex has been reported. The present alkylperoxo complex **3** is the first example of a structurally characterized Mn(II) peroxo complex, and the existence of Mn(II)−dioxygen species is evidenced by our successful characterization of **3**. In biological systems, Mn(II)−dioxygen species such as Mn−O$_2^-$ and Mn−OOH$^-$ are proposed to be an intermediate of the dismutation of superoxide anion (O$_2^-$) by Mn−SOD[19] and H$_2$O$_2$ by dimanganese-catalase.[10d]

Reactivity of the alkylperoxo complex **3** obtained by the present study turned out to be sluggish with respect to oxidation of exogenous substrates such as PPh$_3$, MeSMe, MeS(O)Me, and hydrocarbons; the highly hindered Bu^t groups of $\mathrm{Tp}^{\mathrm{Bu}^t,\mathrm{Pr}^i}$ might prevent access of the substrates to the Mn center of **3**. Although **3** was stable at low temperature, the $\mathrm{Tp}^{\mathrm{Bu}^t,\mathrm{Pr}^i}$Mn moiety decomposed even at room temperature.

In conclusion, the alkylperoxo complex of divalent manganese has been isolated and characterized successfully by using the hindered hydrotris(pyrazolyl)borate ligand. This alkylperoxo complex has a monomeric structure with the essentially tetrahedral geometry of the divalent manganese ion. The high sterically demanding property of $\mathrm{Tp}^{\mathrm{Bu}^t,\mathrm{Pr}^i}$ rather than its high electron donating ability might render the low-valent metal alkylperoxo complexes isolable.

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Supporting Information Available: Experimental details, summary of X-ray analysis, atomic coordinates, thermal parameters, and bond lengths and angles for **3**·MeCN (12 pages). Ordering information is given on any current masthead page.

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(16) Synthetic procedures and analytical data (including X-ray crystallographic work) for **2** and **3** are provided as Supporting Information.

(17) Both **2** and **3** gave similar broad EPR spectra in 0−5000 G (77 K, CH$_2$Cl$_2$ glass). In UV−vis spectra, the absorption intensity under 500 nm region observed for **3** was higher than that for **2**.

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