# Manganese(IV) oxamato-catalyzed oxidation of secondary alcohols to ketones by dioxygen and pivalaldehyde

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**A new manganese(IV) oxamato complex possessing a bis(μ-oxo)dimanganese core has been synthesized, magnetically and structurally characterized, and found to catalyze the aerobic oxidation of secondary alcohols to ketones with co-oxidation of pivalaldehyde to pivalic acid with good yields and high selectivities.**

Interest in high valent manganese coordination chemistry stems largely from the fundamental role that manganese ion in relatively high oxidation states plays in biological dioxygen activation.[1] Manganese interacts with dioxygen and its reduced derivatives in a variety of enzymes from mononuclear (manganese superoxide dismutase) and dinuclear (manganese catalase or manganese ribonucleotide reductase) to tetranuclear (water-oxidizing complex in photosystem II), making use of the Mn$^{\rm II}$, Mn$^{\rm III}$, Mn$^{\rm IV}$ and, probably, Mn$^{\rm V}$ oxidation states. Once it was recognized that the active site in catalase and the water-oxidizing complex contains oxo-bridged dimanganese cores, considerable effort was devoted to obtaining dimeric manganese complexes which could be structural as well as functional models for this class of metalloproteins.[2] During the last two decades several bis(μ-oxo)dimanganese complexes with different ligand types have been reported, but comparatively scarce are the studies concerning their reactivities and, particularly, their use as oxidation catalysts.[3,4] In fact, the manganese complex in the water-oxidizing center also exhibits oxidation chemistry in its lower oxidation states.[5] Here we report the synthesis and physical characterization,‡ and the crystal and molecular structure§ of the manganese complex $[PPh_4]_4[Mn(opba)(O)]_2\cdot 4H_2O$ **1**, where opba = *o*-phenylenebis(oxamato) ligand, as well as a preliminary investigation of its catalytic oxidation properties with dioxygen.

The structure of **1** consists of centrosymmetric bis(μ-oxo)dimanganese(IV) complex anions, $[Mn_2(opba)_2(O)_2]^{4-}$ (Fig. 1), tetraphenylphosphonium cations and crystallization water molecules. The two crystallographically equivalent manganese atoms adopt a distorted octahedral geometry formed by two amide nitrogen and two carboxylate oxygen atoms from two symmetric related opba ligands ($\mathrm{I} = -x, -y, -z$), each donating one of its NO donor set from oxamato to each of the manganese atom at *cis* sites; the coordination sphere of the manganese atoms being completed by two oxygen atoms from the two *cis*-bridging oxo groups. The short Mn–O(1) and Mn–O(1$^{\rm I}$) bonds of 1.799(4) and 1.797(4) Å, respectively, and the acute O(1)–Mn–O(1$^{\rm I}$) angle of 85.9(2)°, are entirely consistent with a di(μ-oxo)-bridged manganese(IV) complex.[2b] Within the planar $Mn_2O_2$ rhomb, the Mn···Mn$^{\rm I}$ and O···O$^{\rm I}$ distances are equal to 2.631(2) and 2.453(3) Å, respectively. The most interesting structural feature of **1** is, however, the bis-bidentate dinucleating coordination mode of the opba ligand. In fact, the oxamato groups of each opba ligand clamp the two manganese atoms, which are in turn tethered by the phenylene backbone between the amide nitrogen donor set. The phenylene linker forces a twist of the N(1)–C(5) and N(2)–C(10) bonds by 125.1(5) and 127.0(5)°, respectively, resulting in a dihedral angle between the mean planes of the oxamato groups of the opba ligand of 71.7(2)°. This distortion is also reflected in the Mn–N(amide) bond distances [1.986(5) and 2.006(5) Å] which are slightly longer than the Mn–O(carboxylate) ones [1.970(4) and 1.965(4) Å]. This unprecedent situation contrasts with that found for the related mononuclear manganese(III) complex with the 4,5-dichloro-opba derivative where the Mn–N(amide) and Mn–O(carboxylate) bond distances average 1.95 and 1.98 Å, respectively.[6] Within this complex the oxamato ligand adopts an almost planar configuration, and the coordination scheme is the familiar tetradentate $N_2O_2$ one with the ligand occupying the equatorial plane about the manganese atom (*trans* isomer).

We have investigated the capability of this novel dinuclear manganese(IV) complex towards oxidative catalytic transformations of various organic substrates by the combined use of dioxygen and an aldehyde as oxidant.[7] The results obtained for some representative primary and secondary alcohols, both aromatic and aliphatics, are detailed in Table 1. Complex **1** selectively catalyzes the oxidation of 1-phenylethanol to the corresponding ketone, acetophenone, by dioxygen plus pivalaldehyde in dichloromethane solution with good yields, *i.e.*

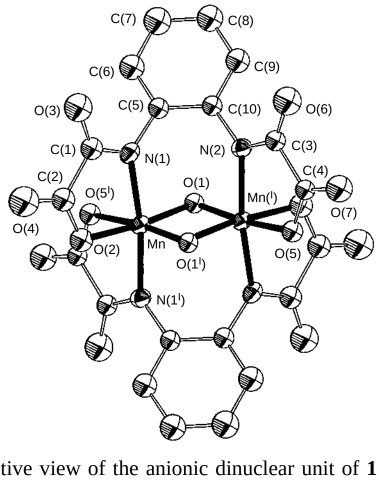

**Fig. 1** Perspective view of the anionic dinuclear unit of **1** with the atom-numbering scheme (thermal ellipsoids are at the 30% probability level and hydrogen atoms have been omitted for clarity). Selected bond distances (Å) and angles (°) with standard deviations in parentheses: Mn–O(1) 1.799(4), Mn–O(1$^{\rm I}$) 1.797(4), Mn–O(2) 1.970(4), Mn–O(5$^{\rm I}$) 1.965(4), Mn–N(1) 1.986(5), Mn–N(2$^{\rm I}$) 2.006(5), Mn–Mn$^{\rm I}$ 2.631(2); O(1)–Mn–O(1$^{\rm I}$) 85.9(2), O(1)–Mn–O(2) 173.0(2), O(1)–Mn–O(5$^{\rm I}$) 93.6(2), O(1)–Mn–N(1) 91.1(2), O(1)–Mn–N(2$^{\rm I}$) 94.9(2), O(1$^{\rm I}$)–Mn–O(2) 93.8(2), O(1$^{\rm I}$)–Mn–O(5$^{\rm I}$) 172.8(2), O(1$^{\rm I}$)–Mn–N(1) 94.5(2), O(1$^{\rm I}$)–Mn–N(2$^{\rm I}$) 91.1(2), O(2)–Mn–O(5$^{\rm I}$) 87.6(2), O(2)–Mn–N(1) 81.9(2), O(2)–Mn–N(2$^{\rm I}$) 92.2(2), O(5$^{\rm I}$)–Mn–N(1) 92.7(2), O(5$^{\rm I}$)–Mn–N(2$^{\rm I}$) 81.8(2), N(1)–Mn–N(2$^{\rm I}$) 172.1(2), Mn–O(1)–Mn$^{\rm I}$ 94.1(2) (symmetry code: $\mathrm{I} = -x, -y, -z$).

**Table 1** Results for the oxidation of alcohols by dioxygen and pivalaldehyde catalyzed by **1**[a]

| Entry | Alcohol | $t$/h | Yield (%)[b,c] |
|---|---|---|---|
| 1 | 1-Phenylethanol | 24 | 70 |
| 2 | 1-(*p*-Methoxyphenyl)ethanol | 24 | 75 |
| 3 | 1-(*p*-Bromophenyl)ethanol | 24 | 68 |
| 4 | 1-(*p*-Trifluoromethylphenyl)ethanol | 24 | 65 |
| 5 | 1-(*p*-Nitrophenyl)ethanol | 24 | 60 |
| 6 | 4-(*tert*-Butyl)cyclohexanol | 48 | 50 |
| 7 | *p*-Methoxybenzyl alcohol | 12 | 95[d] |

[a] Reactions were carried out at room temp. by adding a $CH_2Cl_2$ solution (0.2 $cm^3$) of alcohol (0.11 mmol) to a stirred mixture of metal catalyst ($6.5 \times 10^{-3}$ mmol) and pivalaldehyde (0.33 mmol) in $CH_2Cl_2$ (0.2 $cm^3$) under $O_2$ atmosphere. Consumption of alcohol and formation of ketone during the reaction were monitored by TLC. Obtained ketone and unreacted alcohol were separated by flash column chromatography on silica gel. [b] Yields refer to isolated and pure compounds (column chromatography on silica gel). All compounds exhibited spectral data consistent with their structures. [c] In the absence of metal catalyst some extension of oxidation was observed. [d] Reaction product was exclusively *p*-methoxybenzoic acid.

70% after 24 h (entry 1), with formation of pivalic acid as a coproduct. Moreover, for the series of *para*-substituted phenyl derivatives a small but non-negligible electronic effect is observed, as the substrate with the electron-donating methoxy substituent gives a somewhat higher yield of ketone than that with electron-withdrawing substituents such as trifluoromethyl or nitro groups, *e.g.* 75 *vs.* 60% after 24 h (entries 2 and 5, respectively). For all secondary benzyl alcohols, however, ketones were the only oxidation products as confirmed by $^1$H NMR spectroscopy. Notably, for the oxidation of 4-(*tert*-butyl)cyclohexanol only 4-(*tert*-butyl)cyclohexanone was obtained, and no traces were detected of the corresponding Baeyer–Villiger oxidation product, 4-(*tert*-butyl)caprolactone (entry 6).[8] This observation suggests that the acylperoxy radicals generated *in situ* from the auto-oxidation of the aldehyde are not directly involved as potential oxidizing agents. As expected, under the same reaction conditions used for the oxidation of secondary alcohols to ketones, the primary alcohols give mixtures of both the aldehyde and the acid oxidation products in variable amounts depending on the reaction time, as exemplified by *p*-methoxybenzyl alcohol which leads to almost quantitative formation of *p*-methoxybenzoic acid, *i.e.* 95% after 12 h (entry 7).

Although it is premature to discuss the precise role of the metal complex in the catalytic mechanism at the present stage, it is noteworthy that **1** alone does not lead to alcohol oxidation under stoichiometric conditions and, consequently, involvement of a bis(μ-oxo)dimanganese(IV) species as the active oxidizing agent can also be ruled out. In a typical experiment, complex **1** (0.11 mmol) in dichloromethane (20 $cm^3$) does not react with the more reactive substrate 1-(*p*-methoxyphenyl)ethanol (0.11 mmol) even after a period of three days under stirring at room temperature with or without oxygen atmosphere conditions. That being so, manganese(IV)–acylperoxo or higher valent metal intermediate species, such as manganese(V)–oxo, derived from the oxidation of the bis(μ-oxo)manganese(IV) dimer by the combination of dioxygen and pivalaldehyde, are considered more likely to be responsible for the oxidation in our system. More interestingly, stable manganese(V)–oxo monomeric complexes with amido-containing ligands analogous to that used herein have been isolated and structurally characterized.[9] Attempts to isolate these reactive intermediate species using transition metal ions with more accessible high-valent oxidation states such as chromium are in progress.

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## Notes and References

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‡ *Synthesis and selected data for* **1**: the diethyl ester derivative of the opba ligand (1.54 g, 5 mmol) was dissolved in deoxygenated MeOH (100 $cm^3$), $NMe_4OH$ at 25% in MeOH (8 $cm^3$, 20 mmol) was added to the solution and the resulting mixture was stirred at 60 °C for 15 min under $N_2$. A deoxygenated MeOH solution (50 $cm^3$) of $Mn(ClO_4)_2 \cdot 6H_2O$ (1.79 g, 5 mmol) was then added dropwise *via* a dropping funnel under $N_2$, and a gelatinous light yellow precipitate [presumably a $Mn^{II}$ complex] rapidly formed, together with the crystalline white precipitate of $NMe_4ClO_4$. Addition of 33% aq. $H_2O_2$ (1 $cm^3$, 10 mmol) caused immediate darkening of the solution with concomitant disappearance of the yellow precipitate. The reaction mixture was further stirred at 60 °C for 30 min under $N_2$. The dark-brown solution was filtered to eliminate the solid $NMe_4ClO_4$, and reduced to a final volume of 10 $cm^3$ on a rotatory evaporator. The concentrated solution was treated successively with diethyl ether and acetone to give a black solid which was recuperated in warm water (50 $cm^3$). The resulting mixture was filtered to eliminate solid particles (mainly $MnO_2$), and an excess of $PPh_4Cl$ (3.75 g, 10 mmol) dissolved in the minimum amount of water was then added dropwise to the dark-brown solution under gentle warming. Slow evaporation of the filtered solution in air afforded, after a few days, well shaped large prismatic dark-brown crystals of **1** suitable for X-ray analysis which were filtered on paper and air-dried (60%). Satisfactory chemical analyses obtained (C, H, N, P, Mn). $\nu_{max}/cm^{-1}$ (KBr) 3477vs (O–H) from $H_2O$, 1672 (sh), 1647vs, 1617vs (C=O) and 1403s, 1306s (C–O) from opba ligand, and 643m (Mn–O) from $Mn_2O_2$ ring. $\lambda_{max}$/nm 390 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 10800), 440 (sh) (7080) and 605 (1170) (MeCN). Variable-temperature magnetic susceptibility (Faraday balance, 80–300 K): $J = -158.0\ cm^{-1}$ ($H = -J\, S_1 \cdot S_2$, $S_1 = S_2 = 3/2$).

§ *X-Ray crystal structure analysis*: Enraf-Nonius CAD-4 diffractometer, Mo-Kα, $\lambda = 0.710\,73$ Å, graphite monochromator, 293 K. Lorentz and polarization effects but not absorption correction ($\mu = 3.78\ cm^{-1}$). *Data collection, solution and refinement*: $\omega$–$\theta$, standard Patterson methods with subsequent full-matrix least-squares refinement. SHELX86, SHELX93.[10] $C_{116}H_{96}Mn_2N_4O_{18}P_4$, triclinic, space group $P\bar{1}$, $a = 13.245(3)$, $b = 13.964(3)$, $c = 14.835(3)$ Å, $\alpha = 73.59(2)$, $\beta = 77.98(2)$, $\gamma = 84.60(2)°$, $U = 2572.6(10)$ Å$^3$, $Z = 2$, $D_c = 1.33$ g $cm^{-3}$, $1 \leqslant \theta \leqslant 25°$, crystal $0.15 \times 0.15 \times 0.10$ mm. 6681 reflections measured, 4485 assumed as observed with $I \geqslant 2\sigma(I)$. Refinement on $F^2$ of 651 variables with anisotropic thermal parameters for all non-H atoms gave $R = 0.060$ and $R_w = 0.150$ with $S = 0.936$ (obs. data). CCDC 182/809.

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