Alkane oxidation by a carboxylate-bridged dimanganese(III) complex

Gonzalo Blay,[a] Isabel Fernández,[a] Tomás Giménez,[a] José R. Pedro,*[a] Rafael Ruiz,[a] Emilio Pardo,[b] Francesc Lloret[b] and M. Carmen Muñoz[c]

[a] Departament de Química Orgànica, Facultat de Química, Universitat de València, 46100 Burjassot, València, Spain. E-mail: jose.r.pedro@uv.es

[b] Departament de Química Inorgànica, Facultat de Química, Universitat de València, 46100 Burjassot, València, Spain

[c] Departamento de Física Aplicada, Universidad Politécnica de València, 46071 València, Spain

A new manganese(III) oxamato dimer possesing an unprecedented $Mn_2(\mu-O_2CR)(\mu-OH_2\cdots O_2CR)$ core has been synthesised, structurally and magnetically characterised, and used as a catalyst for the oxidation of alkanes to alcohols and ketones by Bu^tO_2H and O_2 in CH_2Cl_2 at rt.
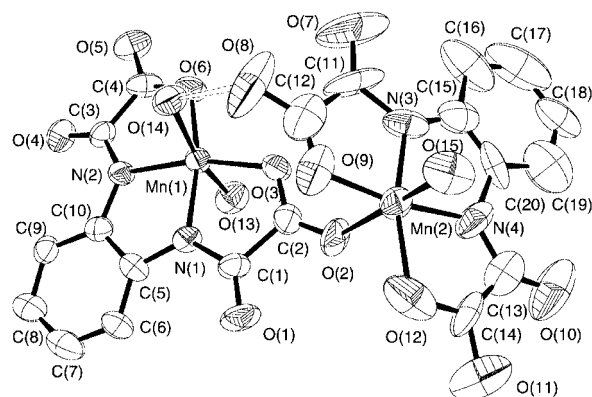
The past two decades have seen a considerable interest in manganese redox enzymes, particularly those containing carboxylate-bridged dinuclear active sites.[1] Among them, the less well understood but functionally important is manganese ribonucleotide reductase (MnRR), which catalyses the dioxygen-dependent reduction of ribonucleotides to deoxyribonucleotides in certain groups of bacteria.[2] This key reaction for the synthesis of DNA initiates, however, with hydrogen atom abstraction from the furanose ring of the ribonucleotide substrate by a tyrosyl protein radical generated during the process of O_2 activation by the dimanganese center.[2c] Although no crystallographic data are yet available for the native manganese enzyme, a manganese-substituted inactive form of the more extensively studied iron ribonucleotide reductase (FeRR) has been isolated and structurally characterised.[3] In this case, two Mn^{II} ions are doubly-bridged by two bidentate carboxylates of glutamato protein residues at a separation of 3.6 Å.[3b] That being so, studies concerning the reactivity of manganese model complexes bearing some structural features similar to those proposed for the different forms of the enzyme can help to understand the mechanism of conversion of ribonucleotides by MnRR.[4] Here we report on the synthesis and general physical characterisation,† crystal and molecular structure,‡ and magnetic properties of the manganese(III) dimer complex $(Ph_4P)_2[Mn_2(opba)_2(H_2O)_3]\cdot3H_2O\cdot MeCN$ **1**, where opba is o-phenylenebis(oxamato). We also report a preliminary investigation of the catalytic activity of **1** towards the oxidation of hydrocarbons with alkyl hydroperoxides in the presence of dioxygen under mild conditions.

The structure of **1** consists of non-centrosymmetric dinuclear manganese(III) complex anions, $[Mn_2(opba)_2(H_2O)_3]^{2-}$ (Fig. 1), tetraphenylphosphonium cations and both water and acetonitrile solvent molecules. The coordination environment about each Jahn–Teller-elongated octahedral manganese atom is formed by two amide nitrogen and two carboxylate oxygen atoms of the tetradentate opba ligand defining the equatorial plane and with the two labile axial positions being occupied by water and/or carboxylate oxygen atoms. In fact, within the dinuclear unit, a carboxylate group from one planar [Mn(opba)] moiety is axially bound to the manganese atom from the other moiety (syn–anti bidentate bridging mode),[5] while a free carboxylate oxygen atom from the latter [Mn(opba)] fragment is hydrogen-bonded to an axial, manganese-bound water molecule of the former fragment [O(8)···O(14) separation of 2.702(9) Å]. This leads to an overall asymmetric doubly-bridged dimanganese(III) core which is reminiscent of the structure of the diiron(III) form of FeRR, but without the oxo bridge present therein.[3a] The $Mn(1)\cdots Mn(2)$ intramolecular separation through this unique nine-membered metallacyclic ring,

$Mn^{III}_2(\mu-O_2CR)(\mu-OH_2\cdots O_2CR)$, in **1** is 5.693(3) Å. This is ca. 2.5 Å longer than the corresponding distance in the related triply-bridged $Mn^{III}_2(\mu-O)(\mu-O_2CR)_2$ species, which have been proposed as suitable structural models of the dimanganese(III) form of MnRR.[6]

The magnetic behaviour of **1** is typical of an antiferromagnetically-coupled dimanganese(III) pair. At room temperature, the product $\chi_M T$ (χ_M being the molar magnetic susceptibility per dinuclear unit and T the temperature) is equal to 6.0 cm^3 mol^{-1} K (6.9 μ_B), a value which is consistent with two Mn^{III} ($S = 2$) ions. Upon cooling, $\chi_M T$ continuously decreases from room temperature to 0.8 cm^3 mol^{-1} K (2.5 μ_B) at 2.0 K, whereas χ_M exhibits a characteristic maximum around 6.0 K, which unambiguously indicates a diamagnetic ground singlet ($S = 0$) pair spin state. The least-squares fitting of the magnetic susceptibility data gives $g = 2.00$ and $J = -2.0$ cm^{-1} (where $H = -JS_1\cdot S_2$; $S_1 = S_2 = 2$). The value of the exchange coupling parameter for **1** compares well with that found for other weakly coupled di(μ-carboxylato)dimanganese(II) complexes (J values of -1.4 and -1.9 cm^{-1}).[7] On the other hand, this certainly weak, although non-negligible, antiferromagnetic coupling through the carboxylate bridge found in **1** emphasises the relative importance of the exchange pathways involving the bridging carboxylate groups for the analysis of the variations in the sign and the magnitude of the exchange coupling in (μ-oxo)di(μ-carboxylato)dimanganese(III) complexes (J values ranging from $+18.0$ to -8.2 cm^{-1}).[6b]

The oxidation catalytic activity of **1** has been examined in a non-coordinating solvent like methylene chloride and at room temperature using tert-butyl hydroperoxide as oxidant under aerobic conditions. The results for some representative alkanes

Fig. 1 Perspective view of the anionic dinuclear unit of **1** with the atom-numbering scheme (thermal ellipsoids are at the 50% probability level and hydrogen atoms have been omitted for clarity). Selected bond distances (Å) with standard deviations in parentheses: Mn(1)–N(1) 1.919(5), Mn(1)–N(2) 1.914(5), Mn(1)–O(3) 1.968(4), Mn(1)–O(6) 1.935(5), Mn(1)–O(13) 2.318(6), Mn(1)–O(14) 2.323(5), Mn(2)–N(3) 1.883(6), Mn(2)–N(4) 1.920(8), Mn(2)–O(9) 1.911(7), Mn(2)–O(12) 2.019(7), Mn(2)–O(15) 2.272(6), Mn(2)–O(2) 2.321(5).

Table 1 Results for the oxidation of alkanes and alkyl arenes catalysed by **1**[a,b]

Entry	Substrate	Product	Yield (%)[c]
1	Cyclohexane	Cyclohexanol	1.9 (3.5)[d]
		Cyclohexanone	2.2 (5.4)[d]
2	Adamantane	1-Adamantanol	8.0
		2-Adamantanol/one	1.0
3	Toluene	Benzaldehyde	3.1
		Benzoic acid	1.3
4	Ethylbenzene	1-Phenylethanol	4.2
		Acetophenone	16.9
5	Diphenylmethane	Benzhydrol	5.2
		Benzophenone	37.3

[a] Reactions were carried out at room temperature by adding a solution of the substrate (0.10 mmol) in CH_2Cl_2 (0.2 mL) to a stirred mixture of the metal catalyst (5.0×10^{-3} mmol) and Bu^tO_2H (0.30 mmol) in CH_2Cl_2 (0.2 mL) under an O_2 atmosphere for a period of 24 h. [b] In the absence of catalyst no oxidation was observed. [c] Yields refer to GLC determination based on the starting substrate. [d] With a reaction time of 72 h.

and alkyl arenes are summarised in Table 1. Complex **1** catalysed the oxidation of cyclohexane to the corresponding alcohol and ketone, cyclohexanol and cyclohexanone, respectively, with varying yields depending on the reaction time (entry 1). Interestingly, the cyclohexanol:cyclohexanone ratio dropped from 0.9 to 0.6 with longer reaction times, suggesting that secondary alcohols are further oxidised to ketones under the experimental conditions. It is also noteworthy that for our catalytic system the tertiary to secondary C–H bond relative reactivities (k_{tert}/k_{sec}; on a per bond basis) for the oxidation of adamantane was as high as 24 (entry 2). On the other hand, alkyl arenes such as toluene, ethylbenzene or diphenylmethane were oxidised selectively at the benzylic position to give the corresponding benzylic oxygenation products, and no traces of the corresponding aromatic ring hydroxylation products were detected by GLC analysis in any case. As expected, the oxidation of toluene gave some minor amounts of benzoic acid together with the main product benzaldehyde, whereas no benzyl alcohol was observed among the oxygenation products (entry 3). The oxidation of ethylbenzene and diphenylmethane afforded mixtures of the corresponding alcohol and ketone exclusively (entries 4 and 5, respectively). The total yields of benzylic oxygenation products followed the trend toluene < ethylbenzene < diphenylmethane (entries 3–5). Indeed, the oxidation efficiency along this series of alkyl arenes $PhCH_2R$ (R = H, Me, Ph) correlates directly with the C–H bond strength, thus suggesting that C–H bond cleavage is the rate-determining step of the catalytic cycle. Further kinetic studies are in progress to determine the detailed mechanism and the exact chemical nature of the active oxidant in these biomimetic oxidations.

Notes and references

† *Synthesis and selected data*: to a solution of the diethyl ester derivative of the ligand (1.54 g, 5.0 mmol) in methanol (50 mL) was added a 25% methanol solution of Me_4NOH (8.0 mL, 20.0 mmol). Solid $Mn(MeCO_2)_3 \cdot 2H_2O$ (1.35 g, 5.0 mmol) was then added in small portions under stirring, and the resulting reaction mixture was further stirred for 15 min at room temperature. A brick-red microcrystalline solid formed abundantly which was collected by filtration and dried under vacuum. The filtered deep brown solution was reduced to a final volume of 25 mL in a rotatory evaporator. Upon standing at 4 °C in a refrigerator, a second crop of crystals separated from the concentrated solution which was also collected and dried (60%). Anal. Calc. for $C_{14}H_{16}MnN_3O_6 \cdot 2H_2O$: C 40.67, H 10.17, N 4.84. Found: C 41.05, H 9.91, N 5.12%. $(Me_4N)[Mn(opba)] \cdot 2H_2O$ (0.83 g, 2.0 mmol) was dissolved in water (50 mL) and the reaction mixture was filtered on paper to eliminate a small amount of solid particles. A solution of Ph_4PCl (0.75 g, 2.0 mmol) in acetonitrile (25 mL) was then added to the filtered deep brown aqueous solution. Well-shaped, brick-red elongated prisms of **1** suitable for X-ray diffraction were deposited after a few hours of slow evaporation at room temperature. They were filtered off and air-dried (90%). ν(KBr)/cm^{-1} 3422s (O–H) from H_2O, 2254w (C≡N) from MeCN, 1669vs and 1645vs (C=O), 1381s and 1280s (C–O) from opba. UV–Vis (MeCN) λ_{max}/nm: 210 (ε/L mol^{-1} cm^{-1} 1.4×10^5), 225 (sh), 260 (4.0×10^4), 275 (sh), 340 (9.4×10^3) and 410 (sh).

‡ *Crystal data for* $C_{70}H_{63}Mn_2N_5O_{18}P_2$: $M = 1434.1$, triclinic, space group $P\bar{1}$, $a = 13.099(3)$, $b = 15.446(3)$, $c = 17.687(4)$ Å, $\alpha = 73.04(3)$, $\beta = 79.94(3)$, $\gamma = 80.84(3)°$, $U = 3348(1)$ Å^3, $T = 293$ K, $Z = 2$, μ(MoKα) $= 0.50$ mm^{-1}, 11 665 reflections measured, 7556 assumed as observed with $I \geq 2\sigma(I)$. Hydrogen atoms were located from a difference synthesis and refined with an overall isotropic thermal parameter. Refinement on F^2 of 875 variables with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.092$ and $wR = 0.251$ with $S = 0.94$ (observed data).

CCDC reference number 166256. See http://www.rsc.org/suppdata/cc/b1/b105132f/ for crystallographic data in CIF or other electronic format.

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