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A novel homodinuclear manganese(III) complex with *N*, *N'*bis(salicylidene)diethylenetriamine: synthesis, structure and catalytic activity

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Abstract

A novel chloride bridged dinuclear manganese(III) complex was prepared and its structure established by X-ray diffraction analysis. The complex showed high selectivity in H_2O_2 promoted oxidation of cyclohexane and cyclic alkenes. Under optimized conditions, 72% of cyclohexane conversion with 85% of selectivity for alcohol was achieved after 5 h. To the best of our knowledge this activity and remarkable selectivity to cyclohexanol is the highst for a manganese catalyst.

Keywords: Homodinuclear; Manganese; Structure; Catalysis; Oxidation

1. Introduction

The design and construction of supramolecular architectures with coordination bonds and hydrogen bonds have attracted great attention in recent years [1]. Among the various families of these supramolecular materials, the family of closed, ring-like coordination complexes such as metallacrowns and metallacycles is an important one, owing to their potential applications in molecular recognition, chiral recognition, catalysis and photoluminescence [2]. According to previous reports, the basic strategy to design these materials is to chelate metal ions by polydentate N,O- or N,N-containing ligands [3]. Multidentate ligands have often been observed to coordinate with more than one metal centre to form infinitely extended structures, such as coordination polymers, polynuclear complexes or metallacycles [4]. The use of a flexible or less-rigid spacer for the construction of a coordination complex has an added advantage as they have many degrees of freedom and a few conformational restraints, which can give various topologies. These types of conformational flexible ligands give unique opportunities to construct novel structures with desirable characteristics.

Selective oxidation of hydrocarbons is of great interest in synthetic organic chemistry and chemical industry for the conversion of petroleum-based feed stocks to more valuable chemicals such as epoxides and alcohols [5]. From both economic and green chemistry perspectives, H_2O_2 and O_2 are the most attractive oxidants because of their high contents of active oxygen species and co-production of only water. Manganese derivatives containing in many cases chelating N-ligands are among the most active catalysts in hydrocarbon oxidations [6]. Mn-salen-type complexes have been extensively investigated for the oxidation of hydrocarbons [7]. It has been also reported that the dinuclear Mn-triazacyclononane complex is the only one which catalyzes the oxidation of alkanes with H_2O_2 in the presence of a carboxylic acid [8]. Selective oxidation of cyclohexane catalyzed by metallic complexes has been reported in the literature [9]; however, the product yields are usually low [9]. Oxidations of cyclohexane that use H_2O_2 in conjunction with cheap, manageable and relatively non-toxic metal-based catalysts are potentially viable for large-scale production. Selected examples of H_2O_2 -epoxidations catalyzed by Mn [10] complexes have attracted much interest, but the search for highly selective environmentally benign alkene epoxidation and alkane C-H bond oxidation methods with aqueous H_2O_2 remains a challenge.

Herein we report on the synthesis, structure and catalytic activity of a novel dinuclear manganese(III) complex with N,N'-bis(salicylidene)diethylenetriamine (H₂saldien). The ligand has often been used in the synthesis of metalorganic complexes [11]. The catalytic activity of the complex was investigated in the oxidation of hydrocarbons with aqueous H_2O_2 as the oxidant without any co-catalyst.

2. Experimental Section

All starting chemicals were commercially available reagents and were used without further purification. The infrared spectrum was taken on a Bruker FT-IR spectrophotometer in the 4000–400 cm⁻¹ region, using KBr pellets. UV/Vis solution spectra were recorded on a thermo-spectronic Helios Alpha spectrometer using a 1 cm quartz cell. The reaction products of the oxidation were determined and analyzed by an HP Agilent 6890 gas chromatograph equipped with a HP-1 capillary column (phenyl methyl siloxane 30 m × 320 μ m × 0.25 μ m) with flame ionization detector. Single-crystal X-ray intensity data were collected on an Oxford Diffraction Xcalibur 3 diffractometer at 173 K (MoK α radiation).

2.1. Synthesis of N,N'-bis(salicylidene)diethylenetriamine (H₂saldien)

Following a literature procedure, the ligand H₂saldien was prepared in high yield and purity [12]. In a typical procedure, to an ethanolic solution of salicylaldehyde (2 equiv.), a solution of diethylenetriamine (1 equiv.) in ethanol was added and the resulting yellow coloured solution was allowed to reflux for 3 h. The excess of solvent was removed under vacuum and a dark yellow coloured oily product resulted. Yield: 85%. IR (KBr, cm⁻¹): 3433 (br, w, O–H), 3317 (w, N–H), 3059 (w), 3009 (w), 1633 (vs, C=N), 1582 (s), 1497 (m), 1461 (m), 1417 (w), 1383 (w), 1337 (w), 1279 (s), 1211 (w), 1151 (w), 1118 (w), 1045 (w), 1025 (w), 973 (w), 894 (w), 850 (w), 755 (s), 641 (w), 566 (w), 461 (w). ¹H NMR (CDCl₃,

250 MHz): δ = 8.213 (2H, -C*H*=N), 6.734-7.227 (8H, aryl), 3.456-3.756 (4H, -CH₂-), 2.605-2.860 (4H, -CH₂-), 1.152 ppm (1H, N-H). ¹³C NMR (CDCl₃, 125 MHz): δ 49.6 (2C), 59.4 (1C), 59.6 (1C), 76.9 (1C), 77.4 (1C), 77.9 (1C), 116.9 (2C), 118.6 (2C), 131.4 (2C), 132.3 (2C), 160.9 (1C), 161.1 (1C), 166.1 (1C), 166.4 (1C). UV/Vis (in CH₃OH, *c* = 1.0×10⁻⁴ mol dm⁻³, λ_{max} [nm] with ε [L mol⁻¹ cm⁻⁴]): 221 (23000), 249 (28000), 327 (9900).

2.2. Synthesis of the homodinuclear manganese(III) complex (1)

A mixture of H₂saldien (0.04 g, 0.14 mmol), manganese(II) chloride tetrahydrate(0.06 g, 0.30 mmol) were placed in the main arm of a branched tube ('branched tube' method) and methanol was added to fill the arms. The tube was sealed and the arm containing the reagents immersed in an oil bath at 60 °C while the other arm was kept at ambient temperature. After 24 h, the black crystals of $[{Mn(Cl)(saldien^{NH})}_2(\mu$ -Cl)]Cl·H₂O·2CH₃OH (**1**) suitable for X-ray analysis were deposited in the cooler arm in yield 72% (0.045 g). Anal. Calc. for C₃₈H₅₀Cl₄Mn₂N₆O₇ (954.53) C 47.81, H 5.28, N 8.80, Mn 11.51. Found C 47.89, H 5.28, N 8.67, Mn 11.40%. IR (KBr, cm⁻¹): 3447 (w, O–H), 3319 (m, N–H), 1611 (s, C=N), 1547(s, δ (NH)). UV-Vis (in CH₃OH, c = 1.0×10⁻⁴mol dm⁻³, λ_{max} [nm] with ε [L mol⁻¹cm⁻¹]): 227 (29000), 245 (26000), 270 (15400), 296 (9200), 370 (3800), 598 (100).

2.3. Catalytic oxidation

The liquid phase catalytic oxidations were carried out under air (atmospheric pressure) in a 25 mL round bottom flask equipped with a condenser and immersed in a thermo stated oil bath. In a typical experiment, H_2O_2 (3 mmol) was added to the flask containing the catalyst (1.03 µmol) and alkene (1.0 mmol) in a solvent (3 mL) and *n*-octane/or chlorobenzene (0.1 g) as internal standard. The course of the reaction was monitored at periodic intervals using a gas chromatograph equipped with a capillary column and a flame ionization detector. The oxidation products were identified by comparison of their

retention times with those of authentic samples. The conversion was determined by the following equation

 $%Conversion = \frac{[(A (substrate)/A(standard)]_{t=0 h} - [(A (substrate)/A(standard)]_{t=x h}]}{[(A (substrate)/A(standard)]_{t=0 h}]}$

A = peak area in GC chromatogram

2.4. Titrimetric analysis for the determination of chloride (Mohr procedure)

In the titration of a neutral solution of chloride ions with silver nitrate [13], a small quantity of potassium chromate solution was added to serve as indicator. At the end point the chromate ions combine with silver ions to form the sparingly soluble, red, silver chromate. Aqueous solution of the fresh complex 0.010 M was titrated with aqueous solution of 0.1 mol/L AgNO₃ in the presence of a few milliliters of dilute potassium chromate solution (0.003 M). The results showed the presence of only one equivalent chloride ions. For determination of chloride after catalysis, the mixture of reaction solution (complex 1 (0.02 g), cyclohexene (1.0 mmol), *n*-octane (0.1 g), acetonitrile (3 ml), H_2O_2 3 mmol, temperature 80 °C) after 5 h was diluted to 25 mL with water and then titrated with the aqueous solution of AgNO₃ in the presence of potassium chromate. The results showed the presence of four equivalents chloride ions.

2.5. X-ray structure determination

A suitable single crystal of **1** was carefully selected under a polarizing microscope and X-ray diffraction data for **1** were collected at 173(2) K on a X Calibur diffractometer using mirror collimated Mo-K α radiation ($\lambda = 0.71073$ Å, graphite monochromator). The structure was solved by Direct Methods with SIR97 [14] and refined with full-matrix least-squares techniques on F^2 with SHELXL-97 [15]. The crystal data and refinement parameters are presented in Table 1. N-bound H-atoms were refined freely,

C-bound H-atoms constrained, methanol- and water-bound H-atoms not considered; a split model has been applied for the refinement of disordered methanol; the free chloride ion is disordered over two sites (occupancy sum 0.5, occupancy ratio ca. 2/1) close to a water O-atom (occupancy fixed to 0.5). The structure plots were prepared with DIAMOND [16]. The structural data has been deposited with the Cambridge Crystallographic Data Center (CCDC-number 939700). These data can be obtained free of JUSCR charge via www.ccdc.cam.ac.uk/data request/cif.

3. Results and Discussion

The Schiff base ligand H₂saldien was synthesized by the dicondensation of diethylenetriamine with 2 equiv. of salicylaldehyde in ethanol [17]. IR and NMR spectra of H₂saldien confirmed that the reaction of diethylenetriamine with salicylaldehyde occurred by the Schiff condensation between the C=O and the NH₂ groups. The manganese complex $[[{Mn(Cl)(saldien^{NH})}_2(\mu-Cl)]Cl \cdot H_2O \cdot 2 CH_3OH (1)$ was prepared by treating a methanolic solution of H₂saldien with an equimolar amount of MnCl₂·4H₂O, where saldien^{NH} denotes the amine protonation (Scheme 1). The Mn(II) was oxidized to Mn(III) by air during the reaction. In the IR spectrum, the free ligand H₂saldien shows stretching bands attributed to phenolic C-OH, C=N, and N-H at 1279, 1633 and 3317 cm⁻¹, respectively. A band at 3412 cm⁻¹ is assigned to v(O-H) vibrations involving intramolecular hydrogen bonding, while a band at 1214 cm⁻¹ is attributed to δ (O-H) (phenolic) [18]. The presence of v(OH) observed for H₂saldien as a weak band at 3433 cm⁻¹ suggests intramolecular hydrogen bonding (O-H···N) in the ligand. For complex 1 the absence of the δ (O-H) (phenolic) band and red shift in azomethine (C=N, 22 cm⁻¹) bands compared to the free ligand H₂saldien indicate coordination of $(saldien)^{2}$ through the phenolate oxygen and azomethine nitrogen atoms in complex 1. As a result of complexation, the UV-Vis spectrum in methanol shows absorbance bands at 227 (29000), 245 (26000), 270 (15400), 296 (9200), 370 (3800),

598 (100) (Fig. 1). The complex shows an UV-Vis spectrum similar to the Schiff base ligand. Based on their extinction coefficients absorbance bands can be assigned to intraligand $\pi \to \pi^*$ (227, 245 nm) and $n \to \pi^*$ (270, 296 nm) transitions (from the azomethine (CH=N) group [19]). The spectrum of the complex shows an intense band in the high-energy region at 370 nm which can be attributed to charge transfer (LMCT) transition. Furthermore, complex 1 shows a ligand field *d*-*d* transition at 598 nm (the inset in Fig. 1).

The molecular structure of the cation with numbering is depicted in Fig. 2. The compound consists of a dinuclear C₂-symmetric [{Mn(Cl)(saldien^{NH})}₂(μ -Cl)]⁺ cation, a chloride counter ion and solvate water and methanol molecules. Selected bond lengths and angles are presented in Table 2. The complex crystallizes in the space group C2/c. The Mn(III) atoms are coupled by both doubly l-phenolato oxygens and the imine nitrogen atoms of the Schiff base ligand and simultaneously one chloride anion in the anti-anti bridging mode. The coordination geometry around the Mn(III) centres may be regarded as distorted octahedral. The equatorial plane is formed by the two imine nitrogen atoms [N(1), N(2)] and two phenolic oxygen atoms [O(1), O(2)] coming from the two ligands, N1 and O1 belong the one Schiff base ligand but N2 and O2 belong the other ligand. $[N2-Mn1-N1 = 169.98(9)^{\circ} \text{ and } O2-Mn1-O1 =$ 177.04(9)°]. The apical positions are occupied by a terminal chloride [Mn-Cl1 = 2.5336(9) Å] and a bridging chloride located on the C_2 axis within the metallacycle [Mn–Cl2 = 2.8236(6) Å, Cl1–Mn2–Cl2 = $170.50(2)^{\circ}$]. The Mn1-imine nitrogen [2.043(2) and 2.044(2) Å] as well as the Mn1-phenolic oxygen [1.852(2) and 1.869(2) Å] bond distances are in the range observed for similar systems [20]. In the Schiff base ligand, the N3 atom is protonated (Fig. 2). The Mn-Mn distance within a cation is 5.1334(5) Å. Within the metallacyclic cation intramolecular π -stacking is observed between the aryl ring plane of C13/C14/C15/C16/C17/C18 and C13ⁱ/C14ⁱ/C15ⁱ/C16ⁱ/C17ⁱ/C18ⁱ ring with a short centroid-centroid distance of 3.898(3) Å (Fig. 2) [21]. The planes are almost parallel to the C_2 axis along b resulting in a dihedral angle of 1.68(3)°. As a consequence of the strong π -stacking the anellated six-membered chelate ring (involving N2and O2) is significantly more puckered than the other one involving N1 and O1 (puckering amplitudes 0.378(2) Å and 0.207(2) Å, respectively) [22]. One of the two amine (NH_2^+)

hydrogen atoms is involved in a bifurcated intramolecular charge-assisted [23,24] hydrogen bonds with O2 and the bridging Cl2 as acceptors (N3 \cdots O2 2.796(3) Å, N3 \cdots Cl2 3.255(3) Å), while the other one is bound to the disordered free chloride ion and water molecule.

Complex $[{Mn(Cl)(saldien^{NH})}_2(\mu$ -Cl)]Cl·H₂O·2CH₃OH(1) is a stable chloride-bridged dinuclear manganese complex in the solution and ligand (saldien^{NH})²⁻ remains coordinated to manganese centres; however, the bridged and terminal coordinated chlorides are separated from the complex during the catalysis. In the UV-Vis spectrum of the complex after catalysis (Fig. 1), absence of the charge transfer band at 370 nm suggests dissociation of the chloride ligands during the catalysis (see below). This finding was also supported by measuring the chloride ions in the solution. Titration of the fresh dinuclear complex **1** solution with AgNO₃ showed the presence of only one equivalent Cl while for the complex after catalysis four equivalents of chloride ions were titrated [13].

In order to explore the catalytic feature of **1** the catalytic oxidation of cyclooctene with hydrogen peroxide was studied in the presence of **1**. All reactions were carried out with 1 mmol of ciscyclooctene in CH₃CN and in the presence of complex **1** at 80 °C. cis-Cyclooctene oxide was the sole product. The results of control experiments revealed that the presence of catalyst (Table 3, entry 1) and oxidant are essential for the oxidation. The catalyst showed high activity in the oxidation of ciscycloocetene in acetonitrile with a high conversion value (65%), affording with excellent selectivity (>99%) the epoxide (Table 3, entry 2). The reaction medium showed remarkable influence on the activity of **1**. No oxidation was observed in CHCl₃ while the conversion values in methanol and ethanol were 11% and 5%, respectively. The highest conversion (65%) was obtained in acetonitrile after 5 h. It was observed that the catalytic activity of complex decreases in the order acetonitrile (relative dielectric constants [25], ($\epsilon/\epsilon_0 = 37.5$) > methanol (32.7) > ethanol (26.6) > chloroform (4.9) (Table 3, entries 2-5). In general, there was a good correlation between the solvent polarity (ϵ/ϵ_0) and the cis-cyclooctene conversion. The highest conversion in acetonitrile possibly is caused by its high dielectric constant. Decreasing the [H₂O₂]/[substrate] molar ratio from 3 to 1 and 2 decreased the conversion to 7% and 18%, respectively (Table 3, entries 2, 6,7). This finding shows partially unproductive decomposition of

hydrogen peroxide by **1**. At temperatures lower than 80 °C the reaction resulted in reduction of the activity of **1** (Table 3, entries 8, 9). Higher temperature probably helps in faster transfer of the oxygen atom from the active intermediate species $[1-H_2O_2]^{\#}$ to the substrate and results in the higher activity.

Furthermore, the catalytic activity of catalyst 1 was examined in the oxidation of cyclohexene and cyclohexane under optimized conditions (H₂O₂/cyclooctene molar ratio = 3, acetonitrile = 3 mL, reaction temperature 80 °C) and the results are summarized in Table 4. Cyclohexene has two fragments accessible for the attack by catalytically active species (the double bond and relatively weak C–H bonds). The comparison of the rates of epoxidation and C–H bond oxygenation could give valuable information on the nature of the oxidizing species. Complex 1 oxidized cyclohexene to the corresponding epoxide with > 99% selectivity. This excellent selectivity in the oxidation of cyclohexene is highly remarkable. In addition, the outstanding catalysis potential of 1 was also observed in the oxidation of cyclohexane (Table 4) with a conversion of 72% resulted after 5 h leading to the products cyclohexanol and cyclohexanoe that were yielded in a ratio of 5.7.

Various homogeneous and heterogeneous mono- and dinuclear Mn-catalysts have been used for the oxidation of cyclohexene to cyclohexene oxide [26,27, 28, 29, 30, 31] and cyclohexane to cyclohexanol/cyclohexanone [27,32,33,26] with H₂O₂ and *t*-BuOOH. There are also interesting and important reports on the epoxidation of various olefins, except cyclohexene, using nonaqueous H₂O₂ (1.2-1.4 equiv.) and acetic acid (14 equiv, to suppress H₂O₂ disproportionation) within 35-90 min at room temperature by a manganese-triazacyclononane catalyst, [Mn(OTf)₂(^{H,Me}PyTACN)] [34], *cis*-dihydroxlation and epoxidation of alkenes with H₂O₂ by carboxylate bridged dinuclear manganese complexes, [Mn₂O(RCO₂)₂(tmtacn)₂] [35], (a carboxylic acid as co-catalyst is necessary for inherent catalase activity of the catalyst and for tuning of the catalyst's selectivity toward *cis*-dihydroxylation and epoxidation of *cis*-cyclooctene to epoxide and cis-diol with H₂O₂ and 2-10 equiv of solid cocatalytic supports by manganese complexes of 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn) supported on carboxylic acid-functionalized SiO₂ [36]. However, none of the reported catalysts shows such a high activity or/and selectivity as complex **1**. Selectivity of the reported [LMn(μ -O)₃MnL][PF₆]₂

catalyst in cyclohexene epoxidation is comparable to **1**. Furthermore, the synthesis of trimethyl-1,4,7triazacyclononane (L) is not as simple as H₂saldien and the presence of a cocatlyst to achieve high activity is necessary by catalyst [LMn(μ -O)₃MnL][PF₆]₂. In the oxidation of cyclohexane, selectivity of **1** with respect to cyclohexanol and its turnover number were higher than those of [LMn(μ -O)₃MnL][PF₆]₂. In addition to the chemical simplicity and easy synthesis of [{Mn(Cl)(saldien^{NH})}₂(μ -Cl)]⁺, it has also the ability to limit the H₂O₂ disproportionation reaction to a great extent relative to most Mn(II)/Mn(III) compounds, the H₂O₂/acetic acid/[LMn(μ -O)₃MnL][PF₆]₂ system (which needs 4.6 to 13.9 equiv. of H₂O₂) [26] and [Mn(μ -terph)(H₂O)₂]_n ([H₂O₂]/[substrate] = 10) (terph = terephthalate) [37]. Despite their power as a synthetic tool and abundant use in academic research, oxidation reactions as a whole comprise as little as 3% of the reactions used on a preparative scale in the pharmaceutical industry [38]. Perhaps the greatest factor influencing the hesitation to employ oxidation reactions on a large scale is the safety of these processes. Using less amount of H₂O₂ improves oxidation process safety in large scale syntheses.

The established intermediate in the catalytic oxidation by Mn complex/H₂O₂ systems is manganese hydroperoxy intermediate, Mn–O–OH, which leads to the formation of Mn(V)-oxo active species [39,40]; the same oxygen atom is subsequently transferred to the substrate in alkane oxidation or olefin epoxidation. Various other high manganese(V)-oxo species based on salen [41], corrole [42], corrolazine [43] and other nitrogen-based ligands have been identified [44]. In the earlier studies the main problem in Mn-salen catalyzed epoxidation with H₂O₂ was the formation of HO[•] radicals by the homolytic cleavage of the weak O–O bond, leading to indiscriminate oxidation [45]. Addition of Lewis bases (cocatalysts), such as imidazole, pyridine, or 2,6-lutidine, was found to favour the heterolytic bond cleavage, leading to reactive manganese-oxo species [46]. The added Lewis bases coordinate axially and facilitate the heterolytic cleavage of the O–O bond in the manganese hydroperoxy intermediate and favour the formation of a catalytically active oxomanganese(V) intermediates [39], which are presumed to be the actual oxidizing species, lead to improvement of the selectivity and catalyst stability [47]. The oxidation reactions are commonly catalyzed by soluble manganese

complexes. However, prevention of H₂O₂ decomposition is one of the major issues with the complexes of Mnⁿ⁺. The major problem of unproductive decomposition of H₂O₂ to H₂O and O₂ by the complexes [48] may in some cases be solved by immobilization of the catalysts [49]. In solution, the mononuclear compounds have a strong tendency to dimerize, and H₂O₂ is readily decomposed by these complexes via Mn–O–O–Mn intermediates. Clearly, the [[{Mn(Cl)(saldien^{NH})}₂(µ-Cl)]Cl complex generates active species upon reaction with H₂O₂, because [[{Mn(Cl)(saldien^{NH})}₂(µ-Cl)]Cl can participate in efficient oxidation as described above. The addition of H₂O₂ to a CH₃CN solution of [[{Mn(Cl)(saldien^{NH})}₂(µ-Cl)]Cl leads to the disappearance of $n \rightarrow \pi^*$ bands and shifts in the $\pi \rightarrow \pi^*$ transitions of the saldien^{NH} ligand (Fig. 3). These findings suggest the formation of an active oxidizing species in the first step by replacing the group Mn^{III}-Cl with Mn^{III}-OOH unit; while saldien^{NH} ligands remain coordinated to manganese centres the coordinated three Cl dissociate in the oxidation medium. Measurements of the chloride ion in the solution of complex 1 and solution of the oxidation reaction medium as well as UV-Vis spectrum of the reaction mixture of [[{Mn(Cl)(saldien^{NH})}₂(µ-Cl)]₂(µ-Cl)]₂(µ-Cl)]₂(µ-Cl)]₂(µ-Cl)]₂(µ-Cl)

Furthermore, one remarkable feature of complex **1** is showing very good catalytic activity merely with 3 equivalents of H₂O₂. Probably, similar to iron(III) complexes [50], in the oxygenation of organic substrates and catalase-like activity there are two different kinds manganese(III)-peroxide adduct in solution (Scheme 2). Unproductive decomposition of H₂O₂ is performed by the adduct I (μ - η ¹: η ¹-peroxo dimanganese(III)) [50] or μ -hydroperoxo dimanganese(IV) which results to the formation of hydroxide bridges on the resulting Mn^{IV} centers [51]. Since the decomposition rate is very low, the concentration of adduct I (or μ -hydroperoxo dimanganese(IV)) must be low. The adduct II (η ¹-hydroperoxide dimanganese(III)) is formed through hydrogen bonding between the hydroperoxide ion and the oxygen atom of the phenoxide group. This type of intramolecular hydrogen bond prevents unproductive decomposition of H₂O₂. A similar η ¹-hydroperoxide intermediate has been assumed for a dinuclear

iron(III) species stabilized through hydrogen bonding between the hydroperoxide ion and the oxygen atom of the amide group [50].

The catalytic performance of the manganese salts $MnCl_2$ and $Mn(CH_3COO)_2$ as homogeneous catalysts have been examined. The manganese salts in CH_3CN solution showed no catalytic activity in the oxidation of alkene with 30% H_2O_2 since hydrogen peroxide was decomposed instantly in the first minutes of the reaction [52]. Since the oxidation of cyclohexene by complex 1 did not stop and continued it suggests that complex 1 is not decomposed in the oxidation medium. The possibility of involvement of dissociated Cl⁻ ions in the catalytic oxidation was excluded by repeating the oxidation of cyclohexene under the optimized conditions and using KCl instead of complex 1 as catalyst which gave no product. Overall, the control experiments provide evidence that the observed catalytic results are derived from precursor of complex 1 and no leaching of the active component and/or demetallation occurs during the catalytic process.

4. Conclusions

A novel chlorido-bridged dinuclear Mn(III) complex was synthesized and successfully used for selective oxidation of cyclohexene, cis-cylooctene and cyclohexane with 3.0 equiv. of H_2O_2 as oxidant in the absence of any cocatalyst. The complex shows comparable and better activity with respect to reported Mn(II) and Mn(III) complexes without requirement to use high equivalents of hydrogen peroxide. To the best of our knowledge the activity and remarkable selectivity to cyclohexanol of **1** is the highest for a manganese catalyst.

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Scheme / Figure / Table captions

Scheme 1. Synthesis of (a) H₂saldien and $[{Mn(Cl)(saldien^{NH})}_2(\mu-Cl)]Cl \cdot H_2O \cdot 2CH_3OH (1).$

Scheme 2. Proposed Mn-hydroperoxide intermediate in the oxidation of hydrocarbons by $[[{Mn(Cl)(saldien^{NH})}_2(\mu-Cl)]Cl/H_2O_2$ system.

Fig. 1. UV/Vis spectra of complex 1, H_2 saldien and complex 1 after 5 h catalytic oxidation of cyclohexene in acetonitril.

Fig. 2. Thermal ellipsoid plot (50% probability) of the cation of $[{Mn(Cl)(saldien^{NH})}_2(\mu -$ Cl)]Cl·H₂O·2CH₃OH (1); hydrogen atoms (except hydrogen atoms of the amine) have been omitted for clarity; bond lengths and angles in Table 2; symmetry transformation i = 1-x, y,0.5–z; intramolecular $\pi \cdots \pi$ interaction (dashed line).

Fig. 3. The visible spectrum of the intermediate formed upon addition of H_2O_2 to a solution of complex **1** in acetonitrile. , AL

Table 1. Crystal data and refinement details for 1.

Table 2. Selected bond distances (Å) and angles (°) for 1.

Table 3. Effect of the catalyst and the amount of oxidant on the oxidation of cis-cyclooctene.^a

Table 4. Oxidation of various hydrocarbons by 1/H₂O₂ in acetonitrile.^a

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PTED MANUSCRIPT













Complex	1
Colour	brown
Net formula	$C_{36}H_{40}Cl_3Mn_2N_6O_4\cdot Cl\cdot H_2O\cdot 2(CH_4O)$
$M_{\rm r}/{ m g}~{ m mol}^{-1}$	954.53
Crystal size/mm	Block, $0.22 \times 0.08 \times 0.07$
Crystal system	Monoclinic
Space group	C2/c
a/Å	18.1184 (19)
<i>b</i> /Å	13.2952 (7)
c/Å	20.132 (2)
β/°	120.715 (14)
$V/Å^3$	4169.2 (6)
Ζ	4
Calc. density/g cm ^{-3}	1.521 (1)
μ/mm^{-1}	0.92 mm^{-1}
Absorpt. correction	multi-scan
Refls. measured	11401
R _{int}	0.048
Mean $\sigma(I)/I$	0.058
θ range/°	4.2-26.4
Observed refls.	3337
x, y (weight. scheme)	0.0511, 6.0103
Hydrogen refinement	a mixture of independent and constrained
	refinement
Refls in refinement	4232
Parameters	281
Restraints	1
$R(F_{\rm obs})$	0.0459
$R_{\rm w}(F^2)$	0.1267
Goodness-of-fit, S	1.061
Shift/error _{max}	0.02
Max electr. dens./e Å ⁻³	0.65
Min electr. dens./e Å ⁻³	-0.60
P	

Table 1. Crystal data and refinement details for 1.

Table 2. Selected bond distances (Å) and angles (°) for 1.

Bond	Length (Å)	Bond	Angle (°)				
Mn1-Cl1	2.5336(9)	Mn1-Cl2-Mn1 ⁱ	130.72(4)				
Mn1–Cl2	2.8236(6)	N1-Mn1-O1	90.51(9)				
Mn1-O1	1.852(2)	N2-Mn1-O2	90.68(9)				
Mn1-O2	1.869(2)	N1-Mn1-O2	91.40(9)				
Mn1-N1	2.043(2)	N1-Mn1-Cl1	94.54(7)				
Mn1-N2	2.044(2)	N2-Mn1-Cl1	95.31(7)	.9			
		O1-Mn1-Cl1	93.24(7)				
Symmetry code $i = 1-x, y, 0.5-z$.							

Entry	H ₂ O ₂ (mmol)	Conv. (%) ^[b]	Selectivity (%)	Time (h)	Temp (°C)	Solvent
1	3	0 ^[c]	-	5	80	CH ₃ CN
2	3	65	100	5	80	CH ₃ CN
3	3	11	100	5	80	МеОН
4	3	5	100	5	80	EtOH
5	3	0	100	5	80	CH ₃ Cl
6	1	7	0	5	80	CH ₃ CN
7	2	18	100	5	80	CH ₃ CN
8	3	32	100	5	25	CH ₃ CN
9	3	45	100	5	60	CH ₃ CN

Table 3. Effect of the catalyst and the amount of oxidant on the oxidation of cis-cyclooctene.^a

^a Reaction conditions: catalyst 1.03 µmol, cis-cyclooctene 1.0 mmol, *n*-octane 0.1 g, acetonitrile

3.0 mL, H_2O_2 3.0 mmol, temperature 80 °C.

^b Conversions based on the starting substrate and determined by GC.

^c In the absence of catalyst 1.

Substrate	Product(s)	Select. (%)	Conv. (%) ^[b] .	TON ^[c]	_
	0	100	65	631	R
\bigcirc	О	100	56	543	<u>R</u>
\bigcirc	ОН	15	72	699	5
		85	1	5	

Table 4. Oxidation of various hydrocarbons by 1/H₂O₂ in acetonitrile.^a

^a Reaction conditions: catalyst **1** 1.03 µmol, substrate 1 mmol, n-octane 0.1 g, acetonitrile 3 mL,

 $\rm H_2O_2$ 3 mmol, temperature 80 °C and reaction time 5 h.

RCCER

^b conversions based on the starting substrate and determined by GC.

^c TON: turnover number = number of moles of product formed per mole of the catalyst.

Highlights

- ✓ Synthesis and structure of a new dinuclear Mn(III) complex of a tetradentate ligand
- \checkmark The complex shows high selectivity in the oxidation of cyclohexene and cyclohexane

ad atalysis

Graphical abstract (picture)



Graphical abstract (synopsis)

Synthesis and structure of a novel dinuclear manganese(III) complex are reported. A remarkable .ata selectivity to the cyclohexanol has been accomplished by the manganese catalyst in the oxidation