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Note

Synthesis, structure and alkene epoxidation activity of an alternating phenoxido and formato bridged manganese(III)–salen complex

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ABSTRACT

One new complex of Mn(III), {[Mn₂(salen)₂(HCOO)](ClO₄)(1.5CH₃OH)(0.5H₂O)]_n (1) has been synthesized and characterized by single-crystal X-ray diffraction analyses. It consists of dinuclear cationic units [Mn₂(salen)₂(HCOO)]^{*}, joined together by weak Mn···O (phenoxido) interactions to form an alternating phenoxido- and formato-bridged 1D polymer. The complex acts as an efficient catalyst in the alkene ((E)stilbene, styrene) epoxidation reaction in presence of the terminal oxidant PhIO in solvents CH₃CN and CH₂Cl₂ independently and it retains its reactivity with high efficiency beyond three cycles.

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1. Introduction

The coordination chemistry of manganese with a diverse range of ligands is an active field of research for decades not only due to their fascinating cluster compounds [1–3], which exhibit unusual magnetic properties [4–5], and the versatile supramolecular arrays [6-8] but also for their suitable biomimetic properties that can mimic the structural features of the active sites of several metalloproteins [9-12] etc. Binuclear phenoxido-bridged manganese(III) compounds containing salen-type Schiff bases are of potential interest due to their easy synthetic methodology and their essential roles in biological systems [13]. Moreover, topical interest in this type of compound has increased since Miyasaka et al. reported a dimeric manganese(III) Schiff base compound, [Mn₂(saltmen)₂ $(\text{ReO}_4)_2$ [[H₂saltmen = N,N'-(1,1,2,2-tetramethylethylene)bis(salicylideneimine)] showing single-molecule magnet (SMM) behavior [14]. Recently our group explored interesting spin-canting behavior exhibited by alternating phenoxido and carboxylato bridged Mn(III)-salen based compounds [15]. As the manganese coordination compounds are a potential source of homogeneous catalysts, we would like to explore the catalytic activity of this type of compounds.

Herein, we report the synthesis, crystal structure, and alkene epoxidation property of a new 1D chain {[$Mn_2(salen)_2(HCOO)$] (ClO₄)(1.5CH₃OH)(0.5H₂O)}_n where *H*₂salen = N,N'-bis(salicylidene)-1,2-diaminoethane. To the best of our knowledge, catalytic activity towards alkene epoxidation of this type of complexes is not reported till date.

2. Experimental

2.1. Starting materials

The reagents and solvents used were of commercially available reagent quality, unless otherwise stated. Styrene and (E)-stilbene were purchased from Aldrich and used in epoxidation experiment without further purification. H_2 salen was prepared by the condensation of salicylaldehyde and 1,2-ethanediamine by reported method [16].

2.2. Caution!

Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

2.3. Synthesis of $\{[Mn_2(salen)_2(HCOO)](ClO_4)(1.5CH_3OH)(0.5H_2O)\}_n$ (1)

A 10 mL methanolic solution of H_2 salen (5 mmol) was added to a methanolic solution (10 mL) of $Mn(ClO_4)_2 \cdot 6H_2O$ (1.805 g, 5 mmol) with constant stirring. After ca. 15 min HCOOH (0.096 mL, 2.5 mmol) was added to the mixture. Triethylamine (0.35 mL, 2.5 mmol) was added drop wise to the solution with constant stirring. The color of the solution turned to dark brown



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immediately. Slow evaporation of the resulting brown solution gave dark brown microcrystalline compound for **1**. The solid was filtered and redissolved in CH₃OH. Layering of the brown methanolic solution with Et₂O gave well formed X-ray quality single crystals.

Complex 1: Yield: 1.41 g; 67%. *Anal.* Calc. for $C_{69}H_{70}Cl_2Mn_4N_8O_{24}$ (1685.99): C, 49.15; H, 4.18; N, 6.65. Found: C, 49.10; H, 4.16; N, 6.60%. IR (KBr pellet, cm⁻¹): 1621 *v*(C=N), 1534 *v*_{as}(C=O), 1441 *v*_s(C=O), *v*(ClO₄⁻), 1098. Magnetic moment μ = 4.09 BM.

2.4. Preparation of iodosylbenzene

This was prepared by hydrolysis of the corresponding diacetate with aqueous sodium hydroxide as reported in the literature [17]. Freshly prepared PhIO was used in every epoxidation experiment.

2.5. Crystal data collection and refinement

For **1**, 16657 data were collected on a Bruker Smart APEX II diffractometer, equipped with graphite monochromated Mo K α radiation at 150 K, and were corrected for Lorentz-polarization effects. The structure was solved using direct methods with the SHELXS97 program [18]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. In the structure three methanol and one water solvent molecules were located and refined with distance constraints and 50% occupancy. The structures were refined on F^2 using the SHELX197 program [18] to R_1 0.0771 and wR_2 0.2565 for 6396 independent reflections.

2.6. Physical measurements

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra in KBr (4500–500 cm⁻¹) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. The electronic absorption spectra (1000– 200 nm) of the complexes were recorded in CH₃CN with a Hitachi U-3501 spectrophotometer. The ¹H NMR spectra were recorded in CDCl₃ on a Bruker AC300 spectrometer. Room temperature magnetic susceptibility was measured with a PAR 155 vibrating sample magnetometer. The electrospray ionization mass spectrometry (ESI-MS positive) spectra were recorded with a Micromass Qtof YA 263 mass spectrometer.

2.7. Epoxidation of alkenes catalyzed by complex 1

Under nitrogen atmosphere, alkene (0.300 mmol) and catalyst $(1.00 \times 10^{-2} \text{ mmol})$ were treated with 5 cm³ dry acetonitrile or dichloromethane. Afterwards under nitrogen atmosphere iodosylbenzene (0.066 g, 0.300 mmol) was added to the solution. ¹H NMR spectroscopy was used for identification of the product. For ¹H NMR experiments epoxides were prepared following the procedure described by Kochi and co-workers [19] when PhIO was used as oxidant.

3. Results and discussion

3.1. IR and UV-Vis spectra of complex 1

In the IR spectra of complex **1**, the moderately strong and sharp band at 1620 cm⁻¹ is assigned to the azomethine v(C=N) group. The strong bands at 1578 and 1441 cm⁻¹ are likely due to the antisymmetric and symmetric stretching modes of carboxylate group, respectively [20]. The characteristic strong peaks for stretching vibrations of uncoordinated perchlorate anion have been observed at 1095 cm⁻¹. A broad band at around 3436 cm⁻¹ is due to the solvent methanol and water molecules. The electronic spectra of the complex in CH₃CN and CH₂Cl₂ solution and solid state diffuse reflectance spectra are shown in Fig. 1. A single absorption band was found at \sim 405 nm in the visible region for **1** in both CH₃CN and CH₂Cl₂ solutions and a broad absorption band is observed in the same wavelength region in solid state, as usually observed in octahedral Mn(III) complexes [21,22]. But, the nature of the absorption band in solid is different from that in solution which indicates that the structural identity is lost on dissolution. This phenomenon was further supported by electrospray ionization mass spectrometry.

3.2. Description of the structure

The structure contains $[Mn_2(salen)_2(OOCH)]^+$ cation together with a discrete perchlorate anion and one water and three methanol molecules (all the solvent molecules with 50% occupancy) in the asymmetric unit as shown in Fig. 2 together with the atomic numbering scheme in the metal coordination spheres. Selected



Fig. 1. Left: UV-Vis spectra in CH₂Cl₂ (A) and CH₃CN (B). Right: UV-Vis spectra in solid state.



Fig. 2. The dimeric structure of 1 with ellipsoids at 30% probability. Solvent molecules have been removed for clarity.

bond lengths and angles are summarized in Supplementary Table 2.

Within the asymmetric unit both metal atoms can be considered as five-coordinate with square pyramidal (4+1) environments taking into account only the five strong bonds. However, both have weak bonds in the other axial position which make the effective coordination number six with tetragonal geometry and allow the formation of 1D chain. The two metal atoms Mn(1)and Mn(2) are coordinated by the four donor atoms of the deprotonated tetradentate Schiff base ligand (salen) in the equatorial sites. The bond lengths are as expected with Mn–O and Mn–N in the ranges 1.852(6)-2.692(6) Å and 1.951(7)-1.978(7) Å respectively. The two oxygen atoms O(1) and O(3) of the bridging formate coordinate to the axial positions of Mn(1) and Mn(2) at distances of 2.142(6) and 2.114(6) Å respectively to form a syn-anti formate bridge between the two Mn ions. These axial bonds are significantly longer than the equatorial bonds as expected for a Jahn-Teller distortion of Mn ions in the +3 oxidation state.

The r.m.s. deviations of the four basal donor atoms from their mean plane are 0.036 and 0.033 Å around Mn(1) and Mn(2) respectively. The Mn(1) and Mn(2) atoms deviate from the respective mean plane by 0.161(1) and 0.213(1) Å, respectively in the direction of the bridging axial formate oxygen atom. The equatorial planes formed by four basal donor atoms around Mn(1) and Mn(2) intersect at an angle of 51.90(3)°.

In addition to these five bonds, the metal atoms show weak interactions in the other axial position to phenoxido oxygen atoms of salen from the neighboring dinuclear units with Mn(1)-O(30) 2.692(2)Å (-x, -y, -z+1) and Mn(2)-O(31) 2.945(6)Å (-x, -y+1, -z+2) thus forming centrosymmetric bridging arrangements as shown in Fig. 3. These two alternating bridging systems i.e. phenoxido- and *syn-anti* formate constitute the 1D chain of the compound.

The crystal packing of the complex is further stabilized by offset or slipped stacking π - π interactions observed between the phenyl rings of phenoxido bridged dimeric units as shown in Fig. 4. The formate bridged dimeric units are stacked with each other by phenyl rings [ring $R_1 = C(12)-C(13)-C(14)-C(15)-C(16)-C(17)$ with ring $R_2 = C(24)-C(25)-C(26)-C(27)-C(28)-C(29)$] having centroidcentroid distance of 3.725(6) Å. The π - π interactions are quite strong because the dihedral angle between the rings is 13.62° with



Fig. 3. A view of polymeric structure of complex **1**. (symmetry element ' = -x, -y, -z + 1).

a slip angle is 20.30°. Similarly the phenyl rings R_3 [C(32)–C(33)–C(34)–C(35)–C(36)–C(37)] and R_4 [C(44)-C(45)–C(46)–C(47)–C(48)–C(49)] are also stabilized by π – π interactions having a centroid–centroid distance of 3.696(5) Å whereas the dihedral angle between the rings is 6.93° with a slip angle of 21.16°.

A search of the CCDC database shows six compounds similar to complex **1**. Among these, a formato bridged complex in which unsymmetrical Schiff base, uspen (H₂uspen = 2-{[2-(3-Hydroxy-1-methyl-but-2-enylideneamino)-ethylimino]-methyl}-phenol) and salen form 1D chain {[{Mn(salen)}{Mn(uspen)}(HCOO)](ClO₄)}_n [23]. Rest of the complexes are based on symmetrical tetradentate Schiff base ligands. Of which, compounds [Mn₂(salen)₂(CH₃₋ COO)]ClO₄ [24] and [Mn₂(7-Me-salen)₂(CH₃COO)]ClO₄ [25] are reported to be acetate-bridged dimers. The association of the dimeric units via the phenoxido bridge of any of these two complexes was not analyzed, although the deposited CIF associated with the reference [24] reveals that it is a 1D polymer like the others [15] with long Mn–O(phenoxido) distances, 2.453 and 2.686 Å, respectively involving the vacant axial positions of Mn(III). The corresponding distances are 2.543(2) and 2.743(3) Å in {[Mn₂(salen)₂ (C₆H₅CH=CH-COO)](ClO₄)}_n [15] and, 2.576(4) and 2.729(4)Å $\{[Mn_2(salen)_2(C_6H_5CH_2COO)](ClO_4)\}_n$ [15]. Since the Mn–O distances are within the bonding distance [26], all of these compounds should be considered as 1D polymer. However, the relatively long $Mn \cdots O$ distance [3.621(2)Å] { $[Mn_2(salen)_2(C_6H_5COO)](ClO_4)_2$ [15] restricts the structure to tetranuclear units. In the present complex, the Mn–O(phenoxido) distances [2.692(2) and 2.945(6) Å] are rather long. However, even the longer Mn \cdots O distance (2.945(6)Å) is reported to be within the Mn...O bonding distance [26]. Therefore the structure is considered as 1D polymer rather than a tetramer.

3.3. Olefin epoxidation catalyzed by complex 1 in presence of terminal oxidant PhIO

Complex **1** is soluble in both CH_3CN and CH_2Cl_2 . Hence, its catalytic activity towards alkene (e.g. (E)-stilbene and styrene) epoxidation reaction has been investigated in CH_3CN and CH_2Cl_2 solvents at room temperature. In both of these solvents, complex **1** produces a brown color solution after dissolution. The color is intensified on addition of the terminal oxidant, PhIO. When substrates (alkenes) are added, the color starts fading and on stirring the solution for ca. 2 h when complete consumption of the substrates is assumed, the intensity of the solution again increases to its original value, indicating completion of alkene epoxidation and the catalyst regeneration. The formation of epoxides was confirmed by the appearance of the characteristic peak in the ¹H NMR



Fig. 4. Supramolecular π - π stacking interaction between the phenyl rings of complex **1**.



Fig. 5. UV–Vis spectral pattern of complex 1: (a) 1.00×10^{-3} M solution of complex in dry acetonitrile at 25 °C, (b) after 1 h reaction with PhIO (0.300 mmol) (sample diluted by fivefold) and (c) after 1 day of the reaction (sample diluted fivefold).

spectroscopy of the resultant products (Supplementary Figs. S2 and S3).

Supplementary Table 3 shows the maximum isolated yield (%) for (E)-stilbene and styrene epoxidation. On comparing the yield of oxidation it may be stated that solvent plays a crucial role in the alkene epoxidation process – the isolated yields of (E)-stilbene (86% in CH₃CN and 72% in CH₂Cl₂) and styrene epoxide(43% in CH₃CN and 37% in CH₂Cl₂) (Supplementary Table 3) indicate that CH₃CN is a better solvent than CH₂Cl₂ for epoxidation of both the substrates.

In recent years, a few similar studies on epoxidation activity of olefins catalysed by Mn(III)–salen complexes were undertaken by several groups. For example, Kochi and co-workers have shown that various types of olefins, including substituted styrenes, stilbenes, and cyclic and acyclic alkenes, are epoxidized in 50–75% yields [19]. Chatterjee and Mitra reported epoxidation of cyclohexene, cyclooctene and 1-hexene with relatively lower yield (2–12%) [27]. Yang and Nocera reported epoxidation of 1,2-dihydronapthalene with several terminal oxidants with comparable efficiency [28]. Das and co-workers reported epoxidation of (E)-stilbene and styrene with high yields of corresponding epoxides [11]. Freire and co-workers reported very stable and reusable Mn(III)–salen based catalyst of styrene with high catalytic efficiency [29]. Murray and co-workers reported electrocatalytic epoxidation with dioxygen as terminal oxidant with 48% yield of corresponding olefin

[30]. Previously our group reported the catalytic epoxidation of Mn(III)–salen based compound with comparable activity [23].

To examine the nature of the catalytic process, 1.00×10^{-3} M acetonitrile (5 cm³) solution of complex **1** was treated with 0.300 mmol PhIO. The results for are shown in Fig. 5. It shows spectra before addition of PhIO (a), after 1 h of reaction (b) and after 1 day of reaction (c). PhIO was completely reacted after 1 day in a solution of the complex. After 1 day, complex **1** produced spectrum (c) which is identical to its original one (spectrum (a), Fig. 5) except for the lowering of the intensity. The species which was obtained after 1 day by the reaction of **1** with PhIO, was again treated with fresh PhIO (0.300 mmol) and alkenes. It was found to be as reactive as the initial compound (i.e. complex **1**) and this reactivity was noticed to be retained beyond three cycles.

To have an idea regarding the species distribution in the solutions we recorded the ESI spectra both in CH₃CN and CH₂Cl₂ and found the presence of base peak of Mn(salen)⁺ (ESI⁺): found m/z M⁺ = 320.92; M_{calc} = 321.04) (Figs. S4a and S5a). In this spectra, peak of [{Mn(salen)}₂(ClO₄)]⁺ ((ESI⁺): found m/z M⁺ = 740.77; M_{calc} = 741.03) (Figs. S4a and S5a) was also observed. These two peaks were obtained in both of the solvents. Whereas in CH₃CN solution a peak of solvent coordinated species [Mn(salen)(CH₃-CN)₂]⁺ (ESI⁺): found m/z M⁺ = 403.06; M_{calc} = 403.10) (Fig. S5b) was obtained, but such solvent coordinated species was absent in CH₂Cl₂. Again [{Mn(salen)}₂(HCOO)]⁺ (Fig. S4b) ((ESI⁺): found m/z M⁺ = 686.90; M_{calc} = 687.08) (Fig. S1b) species is found in CH₂Cl₂ solution, but not observed in CH₃CN.

4. Conclusions

This report presents the synthesis of one new salen based Mn(III) complex that forms one-dimensional chain by alternating phenoxido and formato bridge. In the complex, the dinuclear cationic units $[Mn_2(salen)_2(HCOO)]^+$ are joined together by weak Mn···O (phenoxido) interactions and π - π supramolecular interactions. The complex is found to be a good catalyst for alkene epoxidation.

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Appendix A. Supplementary material

CCDC No. 880391 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via

www.ccdc. cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi. org/10.1016/j.ica.2012.10.012.

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