Aust. J. Chem. http://dx.doi.org/10.1071/CH15068

Synthesis, Structure, and Catalytic Epoxidation Property of a New Phenolato and $\mu_{1,1,3}$ -Azido Co-Bridged Polynuclear Manganese(III) Complex Derived from N,N'-Bis(5-methylsalicylidene)ethane-1,2-diamine

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A new phenolato and $\mu_{1,1,3}$ -azido co-bridged polynuclear manganese(III) complex has been synthesised and characterised. The structure of the complex has been confirmed by single crystal X-ray diffraction analyses. The ability of the complex to catalyse the epoxidation of styrene using PhIO or NaOCl as oxidant has been studied. Results show the catalysis to occur efficiently in the presence of PhIO and NaOCl.

Manuscript received: 7 February 2015. Manuscript accepted: 4 March 2015. Published online: 2 April 2015.

Introduction

Metal complexes with Schiff bases as ligands have played an important part in the development of inorganic chemistry. Of the various structures of metal complexes, the rational design and synthesis of polynuclear structures is an area of continuing interest in coordination and supramolecular chemistry.^[1-3] A common strategy for the synthesis of polynuclear structures that involve manganese complexes is to choose the blocking ligand in such a way that the manganese ion remains coordinately unsaturated and thus allows bridging ligands to coordinate the Mn centers. Although many different bridging groups and transition metal ions have been employed for the construction of such species, the Mn^{III}–N₃ system is one of the most popular among synthetic chemists. A variety of manganeseazido complexes with one-, two-, and three-dimensional polymeric structures have been reported, in which a thiocyanate ligand exhibits diverse bridging modes.[4-6]

The oxidation of various olefins catalysed by metal complexes has drawn considerable attention over the last few decades. Manganese(III) complexes have been found to show excellent catalytic activity towards different oxidation reactions.^[7,8] Research on the oxidation of olefins has received special attention because the oxidised products are of great importance in the chemical industry. Recently, we have reported the catalytic oxidation of the thioethers PhSMe and PhSBz using H₂O₂ or cumene hydroperoxide as oxidants with vanadium complexes.^[9] Herein, we report the synthesis, characterisation, and catalytic oxidation properties of a new manganese(III) complex, $[Mn_4L_4(\mu_{1,1,3}-N_3)_2]_n \cdot 2nClO_4$, where H₂L = N,N'-bis (5-methylsalicylidene)ethane-1,2-diamine (Chart 1).

Results and Discussion

Synthesis and Characterisation

The manganese complex was synthesised in a very facile way. 5-Methylsalicylaldehyde, ethane-1,2-diamine, manganese



Chart 1. H₂L.

perchlorate, and sodium azide were mixed in a 2:1:1:1 stoichiometric ratio in methanol and heated to reflux. The Schiff base ligand coordinates readily to the metal centre as is evident from the change in colour of the solution from yellow to deepbrown immediately after the addition. Elemental analysis of the complex is in accordance with the results of single crystal X-ray determination.

IR and UV-Vis Spectra

The complex shows a strong absorption band at 1620 cm^{-1} due to v(C=N). The bands at 1085, 1065, and 1051 cm^{-1} are due to the non-coordinated perchlorate counterion.^[10] The intense absorption observed at 2070 cm^{-1} is due to the stretching vibration of the azide ligands.^[11] The UV-vis (in acetonitrile) spectrum (Fig. 1) was recorded for the complex. The electronic spectrum of the complex shows five bands at 241, 285, 316, 361, and 426 nm. The bands appearing at the low energy side are attributable to $n \rightarrow \pi^*$ transitions associated with the azomethine chromophores. The bands at higher energy arise from $\pi \rightarrow \pi^*$ transitions within the phenyl rings.

Description of the Crystal Structure of the Complex

The complex crystallises in the triclinic space group *P*-1. The complex is a phenolato and $\mu_{1,1,3}$ -azido co-bridged polynuclear manganese(III) complex. The smallest repeat unit contains a tetranuclear manganese cation [Mn₄L₄($\mu_{1,1,3}$ -N₃)₂] and two perchlorate anions, which are shown in Fig. 2. The Mn1 and Mn3 atoms are in octahedral coordination, with the phenolate



Fig. 1. UV-Vis spectrum of the complex.



Fig. 2. The smallest repeat unit of the complex with 30% thermal ellipsoids.

oxygen and imino nitrogen of the Schiff base ligands defining the equatorial plane, and with one end-on azido nitrogen and one phenolato oxygen of another Schiff base ligand defining the axial positions. The phenolato oxygen acts as a bridging group, which coordinates to two symmetry related Mn atoms, with Mn1...Mn1 and Mn3...Mn3 separations of 3.288(2) and 3.315(2)Å, respectively. The azido ligand acts as a $\mu_{1,1,3}$ bridging group, coordinating to three Mn atoms, with Mn1...Mn2, Mn1...Mn4, and Mn2...Mn4 separations of 4.446(3), 5.877(3), and 5.937(3) Å, respectively. The Mn2 and Mn4 atoms are in octahedral coordination, with the phenolate oxygen and imino nitrogen of the Schiff base ligands defining the equatorial plane, and with two azido nitrogens defining the axial positions. The difference for the axial donor atoms comes from the different types of azido nitrogen. For the Mn2 coordination, the axial azido nitrogens act as bridging groups, which coordinate to two different Mn atoms, with Mn2-N9-N10 and Mn2–N12–N13 angles of 105.7(4)° and 131.9(3)°, respectively. While for the Mn4 coordination, the axial azido nitrogens coordinate as terminal groups, with Mn4-N11-N10 and Mn4-N14-N13 angles of 171.9(5)° and 164.6(6)°, respectively. All the octahedral coordinations are elongated, due to Jahn-Teller effects. The axial bonds are much longer than the equatorial ones, indicating they are weakly coordinated to the Mn atom. This is not uncommon for phenolato or azido-bridged polynuclear structures.^[12,13] The average deviation (0.091(1) Å for Mn1, 0.057(1) Å for Mn2, 0.128(1) Å for Mn3, and 0.038(1) Å for Mn4) of the metal centers from the equatorial least-squares planes indicates that the N2O2 cavities afford almost perfect planes to the metal centres.

As shown in Fig. 3, the alternate phenolato-bridged dinuclear [Mn₂L₂] moieties and mononuclear [MnL] moieties are bridged by end-on azido nitrogens to form 1D chains. The chains are further linked through the coordination of the other side of the azido bridges to other mononuclear [MnL] moieties, generating 2D sheets. The perchlorate anions reside in the cavities of the [Mn₄L₄($\mu_{1,1,3}$ -N₃)₂]_n²ⁿ⁺ cations.

Catalytic Epoxidation Results

Epoxidation of styrene by the complex was carried out at room temperature with PhIO and NaOCl as oxidants. The brown



Fig. 3. The phenolato and $\mu_{1,1,3}$ -azido-bridged 2D sheet of the complex.

colour of the solution containing the Mn^{III} complex and the substrate intensified after the addition of oxidant indicating the formation of oxo-metallic intermediates of the catalyst.^[14] After completion of the oxidation reaction of the alkene, the solution regained its initial colour which suggests that regeneration of the catalyst takes place. Because of the insolubility of the iodosylarenes in common organic solvents, we did not attempt to determine the rate law.^[14] The percentage of conversion of styrene, selectivity for styrene oxide, yield of styrene oxide for the complex, and reaction time to obtain maximum yield using both the oxidants are given in Table 1. The results indicate that the complex converts styrene most efficiently in the presence of PhIO and NaOCl. The complex as a catalyst is selective towards the formation of styrene epoxide despite the formation of byproducts such as benzaldehyde, phenylacetaldehyde, styrene epoxide derivative, alcohols etc.

Experimental

Materials and Methods

Manganese perchlorate, 5-methylsalicylaldehyde, and ethane-1,2-diamine were purchased from Sigma Aldrich and used as received. All other reagents were of analytical reagent grade. Elemental analyses (C, H, and N) were performed using a Perkin–Elmer 240C elemental analyser. IR spectra in a KBr pellet (4500–500 cm⁻¹) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. UV-vis spectra were recorded on a Lambda 900 spectrometer. Gas chromatography (GC) analysis was performed with an Agilent Technologies 6890 N network GC system equipped with a fused silica capillary column (30 m × 0.32 mm) and a FID detector.

Caution! Perchlorate and azide complexes of metal ions are potentially explosive. Only a small amount of material should be prepared, and it should be handled with great care.

Synthesis of the Complex

5-Methylsalicylaldehyde (2.0 mmol, 272 mg) and ethane-1,2diamine (1.0 mmol, 61 mg) were mixed in a methanol solution (50 mL). The mixture was refluxed for 30 min and cooled to room temperature to give yellow precipitation. To the mixture was added solid manganese perchlorate (1.0 mmol, 362 mg) with magnetic stirring. The colour of the reaction mixture changed from yellow to deep brown. Sodium azide (1.0 mmol, 65 mg) was then added to the mixture, and further stirred for 30 min. The filtrate was slow evaporated to give block single crystals. Yield, 27 %. Anal. Calc. for C₇₂H₇₂Cl₂Mn₄N₁₄O₁₆: C 51.47, H 4.32, N 11.67. Found: C 51.30, H 4.55, N 11.83 %. v_{max} (KBr)/cm⁻¹ 2070 v(N₃), 1620 v(C=N), 1540, 1465, 1437, 1377, 1328, 1289, 1222, 1167, 1085 v(ClO₄), 1065 v(ClO₄), 1051 v(ClO₄), 973, 824, 808, 776, 738, 619.

X-Ray Crystallographic Data Collection and Refinements

Single crystal X-ray data for the complex were collected on a Bruker SMART APEX CCD diffractometer. Intensity data were

Table 1. Catalytic epoxidation results

Time [h]	Oxidant	Conversion [%]	Epoxide yield [%]	Selectivity [%]	
				Epoxide	Other
2.5	PhIO	91	78	86	14
3.0	NaOCl	83	65	78	22

collected using graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda 0.71073$ Å) at 298(2) K by ω scan mode. The program $SAINT^{[15]}$ was used for integration of the diffraction profiles. Semi-empirical absorption corrections were applied using the SADABS program.^[16] The structure was solved by Patterson methods using the *SHELXS* program of the *SHELXTL* package and refined by full-matrix least-squares methods with SHELXL.^[17,18] All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 or 1.5 times those of the atom to which they were attached. Crystallographic data and refinement parameters are given in Table 2, and important inter-atomic distances and angles are given in Table 3.

Catalytic Epoxidation of Styrene

The epoxidation reaction was carried out at room temperature in acetonitrile under nitrogen atmosphere with constant stirring. The composition of the reaction mixture was 2.00 mmol of styrene, 2.00 mmol of chlorobenzene (internal standard), 0.10 mmol of the manganese complex (catalyst), and 2.00 mmol iodosylbenzene or sodium hypochlorite (oxidant) in 5.00 mL of acetonitrile. When the oxidant was sodium hypochlorite, the solution was buffered to pH 11.2 with NaH₂PO₄ and NaOH. The composition of the reaction medium was determined by GC with styrene and styrene epoxide quantified by the internal standard method (chlorobenzene). All other products detected by GC were mentioned as others. The reaction time for maximum

Table 2. Crystal data and structure refinement for the complex

Parameter	Complex	
Empirical Formula	C ₇₂ H ₇₂ Cl ₂ Mn ₄ N ₁₄ O ₁₆	
Formula weight	1680.1	
Temperature [K]	298(2)	
Wavelength [Å]	0.71073	
Crystal size [mm]	$0.17 \times 0.15 \times 0.12$	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions		
<i>a</i> [Å]	11.925(1)	
<i>b</i> [Å]	16.356(2)	
<i>c</i> [Å]	21.971(2)	
α [deg.]	96.807(3)	
β [deg.]	101.857(3)	
γ [deg.]	111.205(3)	
Volume [Å ³]	3821.7(7)	
Ζ	2	
$D_{\rm c} [{\rm gcm^{-3}}]$	1.460	
$\mu [\mathrm{mm}^{-1}]$	0.790	
F(000)	1728	
T_{\min}	0.8773	
T _{max}	0.9111	
Index ranges	$-14 \le h \le 13, -19 \le k \le 19,$	
	$-26 \le l \le 26$	
Measured reflections	35394	
Observed reflections $[I \ge 2\sigma(I)]$	6374	
Data/restraints/parameters	13681/0/980	
Goodness of fit on F^2	1.000	
Final <i>R</i> indices $[I \ge 2\sigma(I)]^A$	$R_1 = 0.0775, wR_2 = 0.1559$	
R indices (all data) ^A	$R_1 = 0.2012, wR_2 = 0.2017$	

 ${}^{A}R_{1} = \sum ||Fo| - |Fc|| / \sum |Fo|, \ wR_{2} = \left[\sum w(Fo^{2} - Fc^{2})^{2} / \sum w(Fo^{2})^{2}\right]^{1/2}.$

Table 3. Selected bond lengths and angles

Bond lengths [Å]							
Mn1–O1	1.904(4)	Mn1–O2	1.867(4)				
Mn1–N1	1.970(5)	Mn1–N2	1.979(5)				
Mn1-N9	2.324(5)	Mn1–O1A	2.384(4)				
Mn2–O3	1.878(5)	Mn2–O4	1.879(4)				
Mn2–N4	1.978(6)	Mn2–N3	1.981(6)				
Mn2-N12	2.363(5)	Mn2–N9	2.434(5)				
Mn3–O5	1.855(4)	Mn3–O6	1.902(4)				
Mn3–N5	1.963(5)	Mn3–N6	1.972(5)				
Mn3-N12	2.273(5)	Mn3–O6B	2.477(4)				
Mn4–O7	1.875(5)	Mn4–O8	1.881(4)				
Mn4–N8	1.958(6)	Mn4–N7	1.974(6)				
Mn4–N11C	2.308(7)	Mn4–N14	2.365(7)				
	Bond an	gles [deg.]					
O2-Mn1-O1	96.0(2)	O2-Mn1-N1	173.5(2)				
O1-Mn1-N1	89.9(2)	O2-Mn1-N2	91.4(2)				
O1-Mn1-N2	168.6(2)	N1-Mn1-N2	82.3(2)				
O2-Mn1-N9	97.0(2)	O1-Mn1-N9	92.4(2)				
N1-Mn1-N9	85.4(2)	N2-Mn1-N9	95.3(2)				
O2-Mn1-O1A	94.3(2)	O1-Mn1-O1A	80.5(2)				
N1-Mn1-O1A	84.0(2)	N2-Mn1-O1A	90.3(2)				
N9-Mn1-O1A	167.2(2)	O3-Mn2-O4	94.3(2)				
O3-Mn2-N4	171.3(2)	O4-Mn2-N4	92.1(2)				
O3-Mn2-N3	91.2(2)	O4-Mn2-N3	174.3(2)				
N4-Mn2-N3	82.2(3)	O3-Mn2-N12	94.1(2)				
O4-Mn2-N12	91.3(2)	N4-Mn2-N12	91.6(2)				
N3-Mn2-N12	89.6(2)	O3-Mn2-N9	91.5(2)				
O4-Mn2-N9	85.2(2)	N4-Mn2-N9	83.2(2)				
N3-Mn2-N9	93.4(2)	N12-Mn2-N9	173.6(2)				
O5-Mn3-O6	94.7(2)	O5-Mn3-N5	92.6(2)				
O6-Mn3-N5	167.7(2)	O5-Mn3-N6	172.5(2)				
O6-Mn3-N6	89.4(2)	N5-Mn3-N6	82.3(2)				
O5-Mn3-N12	92.3(2)	O6-Mn3-N12	94.2(2)				
N5-Mn3-N12	95.4(2)	N6-Mn3-N12	93.6(2)				
O5-Mn3-O6B	89.9(2)	O6-Mn3-O6B	82.5(2)				
N5-Mn3-O6B	87.7(2)	N6-Mn3-O6B	84.5(2)				
N12-Mn3-O6B	176.2(2)	O7-Mn4-O8	94.6(2)				
O7-Mn4-N8	172.2(2)	O8-Mn4-N8	91.5(2)				
O7-Mn4-N7	91.7(2)	O8-Mn4-N7	173.7(2)				
N8-Mn4-N7	82.2(3)	O7-Mn4-N11C	97.4(2)				
O8-Mn4-N11C	92.9(2)	N8-Mn4-N11C	87.0(2)				
N7-Mn4-N11C	86.3(2)	O7-Mn4-N14	88.0(3)				
O8-Mn4-N14	94.9(2)	N8-Mn4-N14	86.6(3)				
N7-Mn4-N14	85.3(2)	N11-Mn4-N14C	170.1(2)				

epoxide yield was determined by withdrawing 0.1 mL aliquots periodically from the reaction mixture and this time was used to monitor the efficiency of the catalyst on performing at least two independent experiments. Blank experiments with the oxidant and using the same experimental conditions except catalyst were also performed.

Crystallographic Data

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1039473. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk).

Conclusion

In summary, a new phenolato and $\mu_{1,1,3}$ -azido co-bridged polynuclear manganese(III) complex has been synthesised and characterised by IR and UV-vis spectra. The structure of the complex has also been confirmed by single crystal X-ray diffraction analyses. The complex as a catalyst converts styrene most efficiently in the presence of PhIO and NaOCl with high conversion and selectivity.

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