Synthesis, characterisation and homogeneous catalytic activity study of Mn(II) and Fe(III) ternary complexes

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Abstract

The mixed ligand complexes of the type $LFeACl \cdot nH_2O$ and $LMnA \cdot H_2O$ where L is the mannich base obtained by hydrogenation of Schiff base ligands of salicylaldehyde and amino acids, and A is the bipyridyl or orthophenanthroline synthesised. These complexes were characterised by elemental analysis, spectral, magnetic, FAB mass spectral and electrochemical studies. These complexes have been used as catalysts for epoxidation of olefins like cyclohexene, cis-cyclooctene and norbornene using iodosylbenzene as the oxidant. In the epoxidation reactions using these complexes, it was found that Mn (II) complexes act as better catalysts compared to Fe (III) complexes. The mechanism of the progress of the oxidation reaction and termination of catalytic activity has been investigated by using spectral and electrochemical studies. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Manganese complexes; Iron complexes; Epoxidation; Mannich base; Ternary complexes

1. Introduction

Currently, there is much interest in the transition metal catalysed oxidation reaction as chemical model for the mono oxygenase cytochrome *P*-450 [1,2]. An important goal in this area of research has been to develop catalyst systems for mild and selective oxidations of hydrocarbons [3–5].

The redox potential of the metal centre determines the ease with which the complex goes from one oxidation state to another. In a catalytic oxidation reaction, this means how easily the formation of the catalytically active metal oxo species takes place. Redox potential of the

metal ion in the complex should be moderate so that the oxo species formed is neither unstable nor rigid. This enables the metal oxo species to remain stable until it comes into contact with the substrate and transfer the oxygen easily into it, affecting its oxidation.

The electrochemical property of the metal centre depends on the nature of ligand bound to it [6,7]. In our previous studies, mixed ligand complexes of ruthenium [8], chromium, and iron [9,10] with the ligands dipicolinic acid and aromatic diimines with π donor sites have been prepared and it was observed that ruthenium complexes act as very good catalysts for the epoxidation of olefin. With these in mind, we have synthesised the mixed ligand complexes of Fe(III) and Mn(II) with one tridentate mannich

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base ligand having σ donor coordination sites carboxylate, NH and Phenolate O^- and another π acidic aromatic diamine 22^1 bipyridyl or orthophenanthroline. These complexes were characterised by elemental analysis, electronic and IR spectral, FAB mass spectral, magnetic susceptibility measurement and electrochemical studies. These complexes were used as catalysts for the epoxidation of the olefins like cyclohexene, norbornene and *cis*-cyclooctene.

2. Experimental

2.1. Materials

Salicylaldehyde, α-alanine, l-phenylalanine (Sisco), orthophenanthroline, bipyridyl (Qualigens) $FeCl_3$ anhydrous, $MnCl_2 \cdot 4H_2O$ (Sd fine), and sodiumborohydride (Spectrochem) were used, as received. The tetrabutylammoniumtetrafluoroborate (Fluka) used was of electrochemical grade. The mannich base ligands were prepared by the method reported earlier [11]. Iodosylbenzene was prepared by the method reported by Lucas et al. [12]. All the substrates, norbornene, cyclohexene, *cis*-cyclooctene, and oxidation products norborneneoxide, cyclohexeneoxide, cyclohexene-1-ol, cyclohexene-1-one and *cis*-cycloocteneoxide were obtained from Aldrich and were used as received.

2.2. Physical measurement

The elemental analyses were carried out on a Coleman analyser model-33 and nitrogen was estimated by Duma's method. Manganese and iron were estimated volumetrically. The IR spectra were recorded on a Perkin Elmer spectrophotometer. The UV–visible spectra were recorded on a Shimadzu 240-UV–visible spectrophotometer. Magnetic measurements were carried out by using Gouy's method. The electrochemical unit used consists of model 174A polarographic analyser, universal programmer, x–y recorder, platinum working electrode, platinum wire auxiliary electrode and $Ag/AgNO_3$ reference electrode.

The FAB mass spectra were recorded on a Jeol SX 102/DD 6000 mass spectrometer/Data system using xenon (6 KV, 10 mv) as FAB gas and *m*-Nitrobenzyl alcohol (NBA) as the matrix.

The gas chromatographic analyses were carried out on a Shimadzu G.C. 14B instrument equipped with Oracle 3 computing integrator using 10% SE 30 with 1% QF on chromosorb column (2 M), and nitrogen as carrier gas.

2.3. Synthesis of LFeACl · nH₂O complexes

1 mmol of the mannich base ligand and ~ 2 mmol of lithium were dissolved in 50 ml methanol, and to this was added 1 mmol of $FeCl_3$ in 10 ml methanol, and the reaction mixture was stirred for about one hour. To this, 1 mmol of diimine bipyridyl or orthophenanthroline was added. The reaction mixture was stirred for about one hour and the solid formed was filtered and washed with methanol and dried in vaccuo.

2.4. Synthesis of LMnA · H₂O

1 mmol of $MnCl_2 \cdot 4H_2O$ was taken in 20 ml of 1:1 water–alcohol mixture, and to this was added 1 mmol of diimine bipyridyl or orthophenanthroline in 10 ml 1:1 alcohol–water mixture. The reaction mixture was stirred for one hour. To this was added 1 mmol of mannich base ligand and 2 mmol of NaOH in 30 ml of 1:1 alcohol–water mixture. The reaction mixture was stirred for about one hour and the solid formed was filtered, washed with 1:1 alcohol–water mixture, and then with solvent ether and dried in vaccuo.

2.5. Oxidation of olefins

All the reactions were carried out in a schlenk tube under dinitrogen atmosphere. Olefin (2.5 mmol) catalyst Fe(III) complexes (0.01 mmol)

Table 1
Analytical and magnetic data of the complexes 1–6

Complexes	Analysis found (calculated) %				μ_{eff}
	C	H	N	M (Fe/Mn)	
1.	52.01 (52.3)	3.9 (4.3)	8.6 (9.2)	11.9 (12.2)	5.7
2.	53.9 (54.7)	3.9 (4.3)	8.3 (8.7)	11.2 (11.6)	5.6
3.	60.7 (60.3)	4.6 (4.4)	7.5 (8.1)	10.5 (10.8)	6.0
4.	62.8 (62.1)	4.5 (4.2)	7.3 (7.6)	10.1 (10.4)	5.5
5.	61.6 (62.6)	5.5 (5.1)	7.8 (8.4)	10.6 (11.0)	5.8
6.	64.9 (64.4)	4.9 (4.8)	7.9 (8.0)	10.4 (10.5)	5.9

dissolved in water:acetonitrile (1.3 v/v) or 0.01 mmol of Mn(II) complex in acetonitrile and internal standard chlorobenzene were mixed in the schlenk tube. The reaction mixture was deaerated by flushing with nitrogen for 10 min. Iodosylbenzene 0.5 mmol was added and the reaction mixture was stirred at ambient temperature for about 5 h. 2 μl aliquots were withdrawn from the reaction mixture and analysed by gas chromatography using FID detector. After the 5-h reaction time, there was no further increase in the yield of epoxide indicating that the reaction was complete.

3. Results and discussion

Elemental analyses (Table 1) of the complexes correspond to the expected structure. The structure is shown in Fig. 1.

The IR spectra of the compounds show bands at around 1640 cm^{-1}, 1540 cm^{-1}, and 1520 cm^{-1} indicating coordinated carboxylate group of the mannich base. The $\sqrt{}_{NH}$ band occurs at around 3240 cm^{-1} indicating coordinated NH group. In the complexes 1,2,5 and 6, a broad band at 3300–3500 cm^{-1} is due to the presence of water molecule in the lattice. Other bands corresponding to the mannich base and the aromatic diimines were also seen.

The electronic spectra of all the complexes show intraligand transition bands at 380, 270 and 250 nm. A doublet at 320, 290 nm in the complexes containing bipyridyl and a band at 270 nm in the phenanthroline containing complexes are characteristic of respective tertiary diamines coordinated with metal ion. As expected for Mn(II) complexes, d–d transition bands are not observed in dilute solution because of their being doubly forbidden.
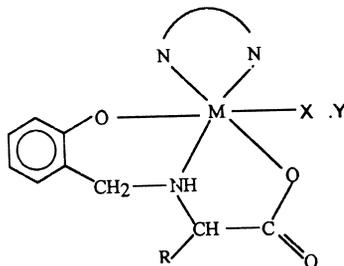
Sr.No.	Complexes	M	R	N͜N	X	Y
1	L^1 FeAX.Y	Fe	-CH$_3$	Bpy	Cl	H$_2$O
2.	L^1 FeAX.Y	Fe	-CH$_3$	Oph	Cl	H$_2$O
3.	L^2 FeAX.Y	Fe	-CH$_2$-C$_6$H$_5$	Bpy	Cl	-
4.	L^2 FeAX.Y	Fe	-CH$_2$-C$_6$H$_5$	Oph	Cl	-
5.	L^2 MnAX.	Mn	-CH$_2$-C$_6$H$_5$	Bpy	H$_2$O	-
6.	L^2 MnAX.	Mn	-CH$_2$-C$_6$H$_5$	Oph	H$_2$O	-

Fig. 1.

In the case of iron complexes the d–d band is observed at ∼ 510 nm in all the complexes. The spectrum is shown in Fig. 2.

The magnetic susceptibility measurements at room temperature show that both Mn(II) and Fe(III) complexes are high spin paramagnetic compounds. Magnetic moment values are shown in Table 1.

The cyclic voltammetric studies of Mn(II) complexes were carried out in acetonitrile medium, using tetrabutylammoniumtetrafluoroborate as background electrolyte. The free ligands do not exhibit any reduction or oxidation peaks in the potential region investigated. The Mn(II) complexes exhibit two peaks in the anodic scan corresponding to Mn(II) → Mn(III) → Mn(IV) oxidation. The potentials have been shown in Table 2, and cyclic voltammogram is presented in Fig. 3a. The reaction is completely irreversible and corresponding reduction peaks were not obtained. The cyclic voltammetric studies of Fe(III) complexes were carried out in acetonitrile–water medium. Two reduction peaks were obtained for complexes 1–3, assignable to Fe(III) → Fe(II) → Fe(I), respec-

Table 2
Electrochemical data for various complexes at 0.1 M electrolyte concentration

Complexes	E_{PC}^1	E_{PC}^2	E_{Pa}^1	E_{Pa}^2
1	−0.42	−0.66		
2	−0.34	0.66		
3	−0.43	−0.79		
4	−0.48	−		
5	−	−	0.20	0.54
6	−	−	0.26	0.61

Solvent for complexes 1–4 is water–Acetonitrile (1:3 v/v).
Solvent for complexes 5 and 6 is Acetonitrile.
Electrolyte, tetrabutylammoniumtetrafluroborate.
Ag/AgNO₃ reference electrode.

tively. In another complex, 4, only one reduction peak is obtained at −0.48 V and this has been assigned to Fe(III) → Fe(II) reduction. In all cases, the electrochemical reactions are completely irreversible. Cyclic voltammogram in case of complex 3 is shown in Fig. 4 and potentials for all complexes are recorded in Table 2.
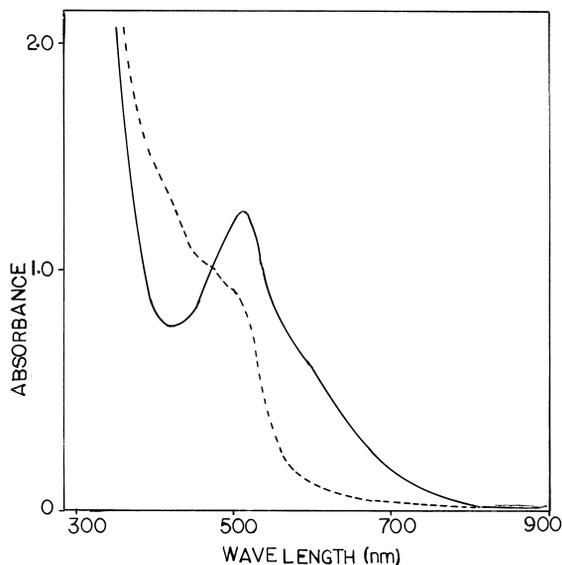

Fig. 2. The electronic spectra of complex 4 (————) after addition of PhIO (---) in water–acetonitrile (1:3 v/v) solvent mixture.
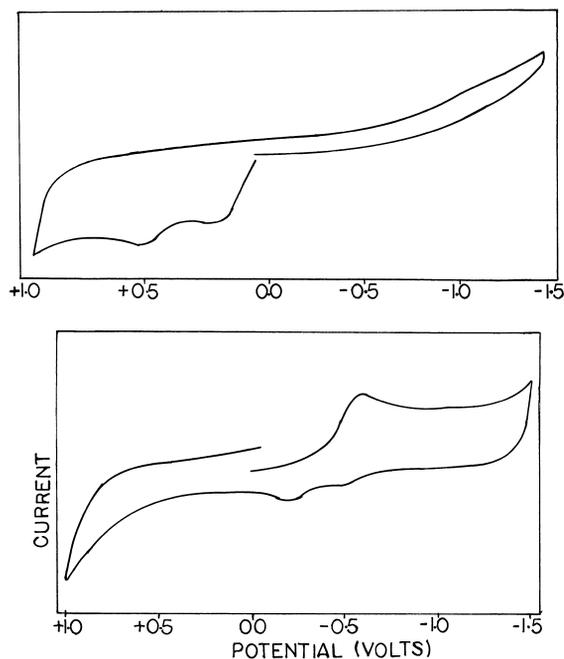

Fig. 3. (a) Cyclic voltammogram of complex 5 in acetonitrile solvent. (b) Cyclic voltammogram of complex 5 after addition of PhIO in acetonitrile.
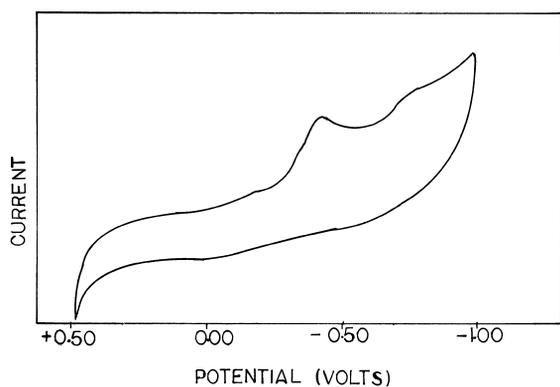
Fig. 4. Cyclic voltammogram of complex 3 in water–acetonitrile with tetrabutylammonium tetrafluroborate (0.1 M) at a platinum electrode and a scan rate 100 mV s^{-1}.

The FAB mass spectra of three complexes LFeAX.Y, L^{2}MnAY and L^{2}FeAX were recorded. The spectrum of complex 1 is shown in Fig. 5. In the mass spectrum of the complex L^{1}FeAX, peak at $m/z = 441$ corresponds to the parent compound L^{1}FeAX, $m/z = 405$ to L^{1}FeA, $m/z = 247$ to L^{1}Fe or AFeX. For the compounds L^{2}FeAX the peak at $m/z = 518$ corresponds to parent ion, $m/z = 481$ to L^{2}FeA, $m/z = 325$ to L^{2}Fe and $m/z = 247$ to FeAX. In case of L^{2}MnAX peak at $m/z = 523$ corre-

sponds to L^{2}MnAX, $m/z = 505$ to L^{2}MnA, $m/z = 320$ to L^{2}Mn and $m/z = 235$ to MnA.

3.1. Catalytic reactions

The results of the oxidation of olefins with iodosylbenzene in the presence of all the complexes have been shown in Table 3. A controlled experiment using *cis*-cyclooctene under identical experimental conditions, but excluding metal complexes, did not give any epoxide. For manganese complex, acetonitrile was used as the solvent; whereas, for the iron complex, water–acetonitrile mixture (1:3 v/v) was used as solvent for the oxidation reaction. Oxidation of norbornene and *cis*-cyclooctene gave corresponding epoxides selectively, whereas cyclohexene gave additional oxidation products other than cyclohexene oxide. The yield of epoxide in the case of manganese complexes was found to be very high as compared to iron complexes. The turnover numbers in the case of manganese and iron complexes were found to be 23–26 and 3–8, respectively, indicating that the reactions are catalytic. The iron complexes show less activity in the epoxidation reaction of the above mentioned olefins.
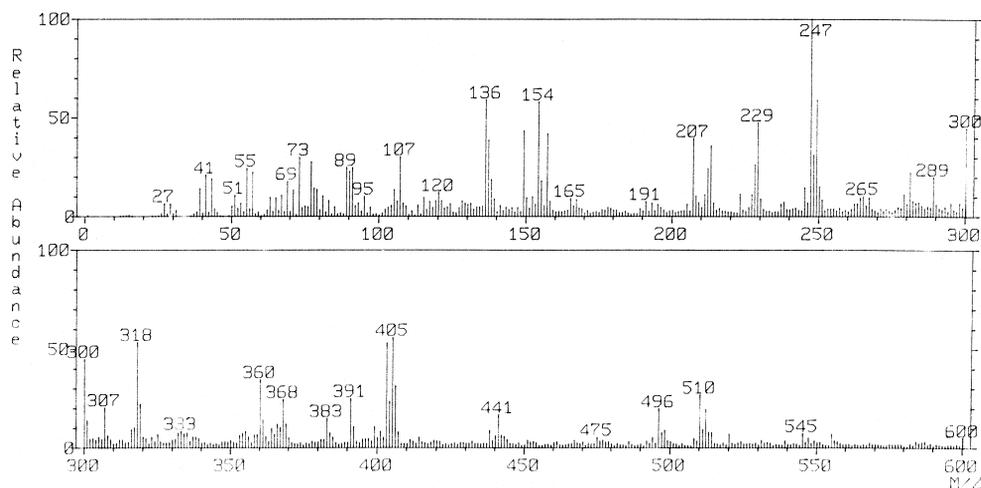

Fig. 5. FAB mass spectrum of complex 1.

Table 3

Olefin	Product	Yield[a] (%) with catalyst					
		1	2	3	4	5	6
Norbornene	Norbornene oxide	7	5	10	10	48	46
cis-Cyclooctene	cis-cyclooctene oxide	5	7	5	4	51	48
Cyclohexene	cyclohexene oxide	4	3	4	3	31	33
	Cyclohexene-1-one	11	10	17	17	7	10

[a] Yield based on Iodosylbenzene charged.

Substrate: oxidant: catalyst, mole ratio 250:50:1; solvents are $H_2O:CH_3CN$ (1:3 v/v) for complexes 1–4, and CH_3CN for complexes 5 and 6.

To suggest the mechanism of the oxidation reaction, the UV–visible spectra of the complexes were recorded in the presence of PhIO. After the addition of PhIO, the colour of the solution of iron complexes changes from violet to light reddish and in the visible spectrum, the original d–d band in the complex reduces in intensity and a new shoulder occurs at around 480 nm. This can be attributed to the formation of metal oxo species.

In the case of Mn(II) complexes, the colour of the solution of the complex turns dark brown but no new peak was observed in the visible region. This may be because the tailing of the charge transfer transition masks the d–d band.

The electrochemical studies were carried out in the presence of PhIO. On addition of PhIO to Mn(II) complexes 5 and 6, the Mn(II) → Mn(III) oxidation peak completely disappears and a new peak occurs at around −0.61 V in the case of complex 5, and −0.57 V in the case of complex 6. The cyclic voltammogram of complex 5 in the presence of PhIO is shown in Fig. 3b. This can be attributed to the reduction of Mn(IV) → Mn (III). On addition of PhIO to the solution of the complex, there is a formation of Mn(IV) = 0 species which acts as an intermediate and transfers oxygen to the olefin. In the case of iron complex, the original peak corresponding to Fe(III) → Fe(II) reduction disappears. However, no new peak is observed on the less negative potential region. This may be because the reduction may be at a more positive potential not attainable in aqueous solution.

The reaction can be explained in terms of oxygen rebound mechanism as reported by Groves and McClusky [13].

In the oxidation reaction of cyclohexene, it was observed that the major product was cyclohexene oxide in the case where manganese complexes were used as the catalyst. However, in the case of iron complexes, the amount of cyclohexene oxide was found to be less and the yield of cyclohexene-1-one was found to be larger.

The termination of the reaction can be mainly because of two reasons, the formation of μ-oxo species or the oxidative degradation of the complex. Electronic spectral or electrochemical study do not show formation of μ-oxo species. Hence, the termination may be because of the oxidative degradation of the complex, where the phenolic oxygen is converted to quinone form, which gets detached from the metal leading to the termination of the catalytic reaction. To confirm this, IR spectrum of the solid, which deposited after the reaction, was investigated. It was found that the IR spectrum of the original complex and that of the solid formed after the reaction differ significantly. A band at 1650 cm^{-1} is observed corresponding to the quinonic C = O. This confirms the degradation of the complexes. It was observed earlier [14] that the mannich base complexes act as less efficient catalysts as the phenolic –OH in the mannich base is known to be more susceptible to oxidation.

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