Study of olefin epoxidation using binuclear Mn(II) complexes as catalyst in presence and absence of UV light

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Abstract

Mn(II) binuclear complexes of Schiff base ligands have been synthesised by the reaction of $MnCl_2 \cdot 2H_2O$ in ethanolic solution with the Schiff base obtained by the condensation of pyridine-2-carboxaldehyde and longer aromatic diamines like 44′ diamino diphenyl, 44′ diamino diphenyl methane and 44′ diamino diphenyl ether respectively. These complexes have been characterised by elemental analysis, spectral, magnetic, electrochemical and FAB mass spectral studies. These complexes have been used as catalyst for the epoxidation of olefin using iodosyl benzene as oxidant. The combined effect of light and catalyst on the catalytic activity have also been investigated. © 1998 Elsevier Science B.V.

Keywords: Binuclear complexes; Epoxidation; Schiff base complexes; Mn(II) complexes

1. Introduction

Selective oxygenation or oxidation of organic substrate is important in the chemical and petrochemical industries [1,2]. Nowadays mimicking enzymatic type activity in simple molecules is of interest in developing catalysts capable of carrying out oxygenation reaction, selectively and under mild conditions [3]. With this in mind, manganese porphyrin complexes have been extensively studied as catalysts in the homogenous catalytic hydrocarbon oxidation reaction [4–10]. In continuation of such studies many Schiff base complexes of manganese have been synthesised, characterised, their oxygen uptake reactions have been studied [10–18] and their efficiencies have been correlated with the redox potentials of the metal complexes. It was observed that the mononuclear complexes are poor in selective oxidation of organic substrates [19,20]. Hence, the study of multinuclear complexes as catalyst occupies an important position in modern inorganic chemistry owing to their selective oxidation property.

The synthesis and catalytic study of binuclear complexes of Mn(II) such as $[Mn_2(pappd)_2]Cl_4$ and $[Mn_2(pampd)_2]Cl_4$, where pappd and pampd are Schiff bases obtained by the condensation of pyridine 2-carboxaldehyde with para-phenylene diamine and metaphenylenediamine, respectively, were carried out in our laboratory and the results were reported [21]. Similarly, the complexes of Fe(III), Cr(III), Ru(III), Mn(II) and Mn(III) with some binucleating amides [22],

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Schiff bases [23–27] and Mannich bases [28] were prepared and their catalytic activities were studied and discussed with reference to the nature of the ligands and metal ion.

It was thought of interest to investigate the role of the length of the bridging ligand which binds the two metal centres, on the catalytic activity of the metal centres. Hence, manganese(II) complexes of the Schiff base derived from pyridine 2-carboxaldehyde and 44′ diamino biphenyl, 44′ diamino biphenyl methane and 44′ diamino biphenyl ether were synthesised and the epoxidation reaction of some olefin substrates were carried out using the complexes as catalysts both in the absence and the presence of UV light. The results of this study are presented in this paper. The synthesis of the complexes and their magnetic studies, cyclic voltammetric studies, UV visible and mass spectral analysis has also been presented in details.

2. Experimental

2.1. Materials

Pyridine-2-carboxaldehyde (Spectrochem) was used as received. 44′ diamino diphenyl (SD Fine), 44′ diamino diphenyl methane and 44′ diamino diphenyl ether (Fluka) were purified before use. Iodosyl benzene was prepared by the method reported by Luccas et al. [29] $MnCl_2 \cdot 2H_2O$ (SD Fine) used was of A.R. grade. All substrates, norbornene, cyclohexene, cis-cyclooctene and the oxidation products norbornene oxide, cyclohexene oxide, cyclohexen-1-ol, cyclohexen-1-one and cis-cyclooctene oxide were obtained from Aldrich and were used as received.

2.2. Physical measurements

The elemental analysis were carried out on a Coleman analyser model-33 and nitrogen was

estimated by Duma's method. Manganese was estimated gravimetrically. 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 using Gouy's method. The electrochemical unit used consists of model 174 A polarographic analyser, a universal programmer, an $X–Y$ recorder, a platinum working electrode, a 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 analysis were carried out on a Shimadzu G.C. 14B instrument equipped with an oracle 3 computing integrator, using 10% SE-30 with 1% QF on a chromosorb column (2M) and nitrogen as carrier gas.

2.3. Synthesis of binuclear complexes

To a solution of pyridine-2-carboxaldehyde (4 mmol in 50 ml ethanol), the diamine solution (2 mmol in 25 ml ethanol) was added and the mixture was stirred for 30 min. To this $MnCl_2 \cdot 2H_2O$ (2 mmol in 30 ml ethanol) was added. The reaction mixture was stirred for 1 h. The solid obtained was filtered and washed with ethanol and dried in vacuum

2.4. Oxidation of olefins

All the reactions were carried out in a Schlenk tube under dinitrogen atmosphere. Olefin (2.5 mmol), catalyst (0.01 mmol) dissolved in a water–dioxan mixture (2:6 v/v) and chlorobenzene (internal standard) were mixed. The reaction mixture was de-aerated by flushing nitrogen for 10 min. Iodosyl benzene (0.5 mmol) was added and the reaction mixture was stirred for about 5 h. 2 μl aliquots were withdrawn from the reaction mixture and analysed by gas

chromatography using a FID detector. After 5 h reaction time there is no further increase in the yield of epoxide. This indicates that the reaction is complete.

The photo reaction was carried out in a double walled schlenk tube of 10 ml capacity. A high pressure mercury vapour (HPMV) lamp was used as a light source. The reaction mixture was stirred magnetically and cooled by water circulation.

3. Results and discussions

Elemental analysis (Table 1) of the complexes corresponds to the molecular formulae I (Mnpadadp)$_2$Cl$_4$ · 2H$_2$O, II (Mnpadadpm)$_2$Cl$_4$H$_2$O and III (Mndadpe)$_2$Cl$_4$ · 2H$_2$O. The complexes can be assigned the structures as shown in Fig. 1.

The IR spectra of the three complexes showed absorption at ∼ 1600 cm^{-1}, i.e. at a lower wave number than that of the free ligand indicating the coordination of the azomethine group C=N. Other characteristic bands of ligands observed are aromatic -c–c stretching between 1550–1350 cm^{-1}. In all complexes a broad band is observed at 3300–3500 cm^{-1} indicating the presence of water molecules in the lattice.

The magnetic susceptibility measurement at room temperature shows that the complexes (I–III) are high spin paramagnetic compounds with a magnetic moment (5.4–6.2 BM).

The electronic spectra of all the complexes shows intraligand bands at 336, 278, 240 and 216 nm. As expected for Mn(II) complexes the
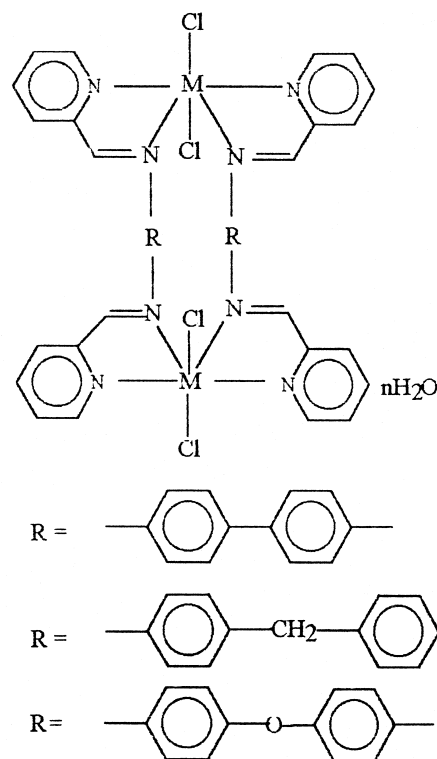

Fig. 1. Structure of complexes.

d–d transition band is not observed in dilute solution. The spectra is shown in Fig. 2.

Cyclic voltametric measurements were carried out for the binuclear complexes in a water–dioxan medium (2:6). It was found that during the anodic scan Mn(II) is oxidised to Mn(III) and the oxidation is found to be irreversible. The oxidation potentials are +0.59, +0.46 and 0.48 V, respectively. The voltammogram is shown in Fig. 3.

The mass spectra of complex II was recorded and m/z = 1018 corresponds to the parent compound (Mnpadadpm)$_2$Cl$_2$H$_2$O. Other fragments obtained are (Mnpadadpm)$_2$Cl$_2$, m/z = 930 and Mn$_2$padadpmCl$_2$, m/z = 550.

3.1. Catalytic reaction

Results of the oxidation studies using the metal complexes (I–III) as catalysts and three

Table 1
Analytical and magnetic moment data of binuclear complexes

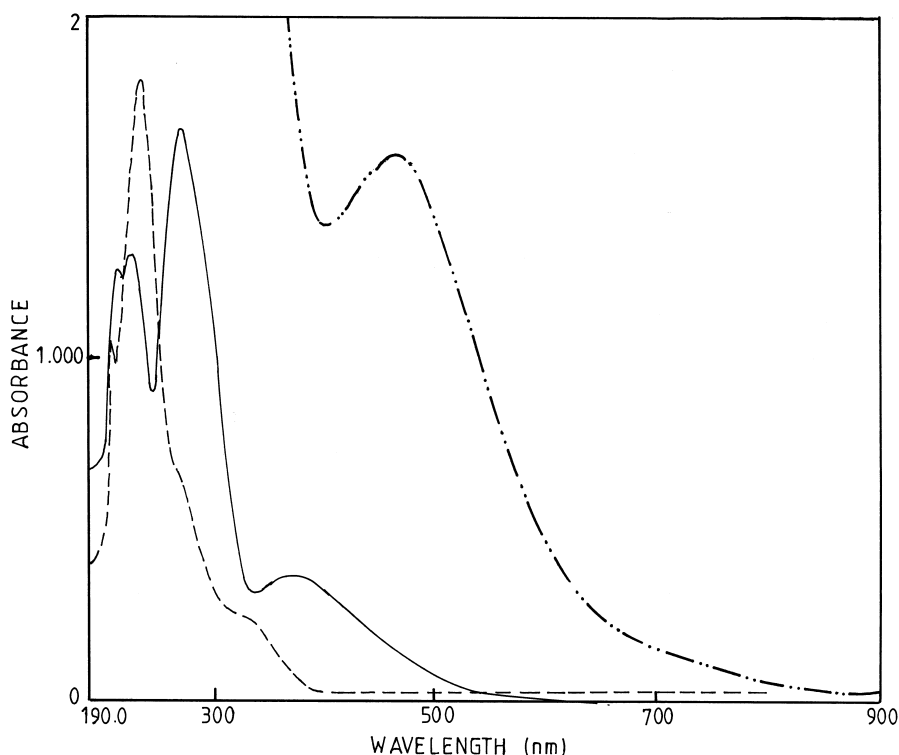| Complexes	Analysis[a]				μ_{eff}
	C	H	N	Mn	
I	57.1 (56.9)	4.1 (3.9)	10.8 (10.9)	10.6 (10.8)	5.4
II	59.2 (58 7)	4.3 (4.3)	11.2 (11.0)	10.4 (10.7)	5.8
III	55.4 (55.2)	4.3 (3.9)	10.7 (10.7)	10.2 (10.7)	6.2

[a]Calculated values in parentheses.

Fig. 2. UV visible spectra of: (- - -) complex II, (————) complex II in the presence of light and (– · · –) complex II in the presence of PhIO in water–dioxan (2:6 v/v).

alkenes is shown in Table 2. It is noticed that in the case of complex I, the catalytic activity is found to be greater than for the other two complexes, II and III. Norbornene and cyclooctene gave the corresponding epoxide selectively. Oxidation of cyclohexene gave cyclohexene oxide together with a small amount of cyclohexen-1-one. The amount of cyclohexene-1-ol formed is negligible. With norbornene the oxidation reactions were studied in the presence of light and it was found that the catalytic activity was same as that for the complexes only. The results are shown in Table 2.

The catalytic activity can be explained by the oxygen rebound mechanism Fig. 4 [31].

In order to support the mechanism of catalytic reaction the electronic spectra of the complexes were recorded after the addition of PhIO. The colour of the solution changes to dark brown and a new band appears in all complexes

which are, respectively, 450, 460 and 460 nm for the complexes I, II and III, Fig. 2. This may be due to the d–d transition in the Mn^{IV} ion and supports the formation of metal oxo species
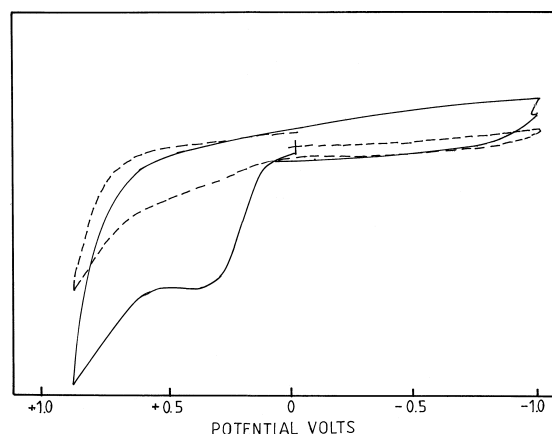

Fig. 3. Cyclic voltammogram of (————) of complex II and (- - -) complex (II) in the presence of PhIO in water dioxan (2:6 v/v) at platinum electrode.

Table 2
Epoxidation of olefins catalysed by complexes [I–III][a] and with complex and light

Olefin	Product	Yield[b] (%) with catalyst		
		I	II	III
Norbornene	norbornene oxide	21	16	19
cis-Cyclooctene	cis-cyclooctene oxide	8	6	8
Cyclohexene	cyclohexene oxide	8	6	7
	cyclohexene-1-one	6	7	8
Norbornene[c]	norbornene oxide	19	15	18

[a] Substrate:oxidant:catalyst mole ratio 250:50:1 solvent water–dioxan (2:6 v/v).
[b] Yield based on iodosyl benzene charged.
[c] Epoxidation in the presence of catalyst and light.

$Mn^{IV}=O$. The appearance of new bands on the addition of PhlO to Mn(III) complexes was reported earlier [27,30] and it was attributed to the formation of $Mn^{V}=O$ species. This indicates that a metal oxo species is formed as a transient species during the oxidation reaction with a mono oxygen donor like Iodosyl benzene.

In order to confirm the formation of $Mn^{IV}=O$ species cyclic voltametric studies were carried out in presence of PhlO and it was found that during anodic scanning the Mn(II)–Mn(III) oxidation peak completely disappears on addition of PhlO. This shows that a new species with different oxidation potentials is formed. However, no new reduction or oxidation peaks were observed. This can be due to the fact that the reduction or oxidation may take place at a potential range which cannot he measured under the given experimental conditions. However, the observation of $Mn^{IV}=O$ species during the UV spectral studies indicates that the disappearance of the anodic peak may be due to the formation of $Mn^{IV} = 0$ in the presence of PhlO.

The termination of catalytic activity may occur because of two factors, due to the formation of Mn–O–Mn species which has poor catalytic activity or due to the oxidative degradation of metal complexes. This was confirmed by taking the IR spectra of the solid which precipitated after the catalytic reaction. The IR spectra of the solids precipitated during the reaction are very much different from that of the IR spectra of the parent compounds, indicating that the complex undergoes oxidative degradation during the catalytic reaction.

It is expected that the length of the bridging ligand will enhance the catalytic activity of the complexes since two metal centres would be then far apart and hence two olefin molecules can be accommodated on two metal centres without much steric hindrance. The transfer of oxygen to the two substrate molecules is facilitated. However, in the present study it is observed that compared to $(Mnpappd)_2Cl_4$ and $(Mnpampd)_2Cl_4$ complexes, reported earlier [21], the catalytic activity is observed to be slightly less, though the two metal ions are more separated in the present complex catalysts. This can be due to some orientational factor in the bridging ligand which hinders the easy approach of the substrate, thereby making oxygen transfer to the substrate very difficult. Another possibility is that the lengthy bridged group may be susceptible to rapid oxidative degradation.

Recently in our laboratory it was found that in the presence of a catalyst and UV light the catalytic activity is enhanced due to independent catalytic effects of the complex and light [32]. Hence, in this system we have also carried out the experiment in the presence of light and a catalyst and it was found that the yield was nearly the same as that for the catalyst alone. In
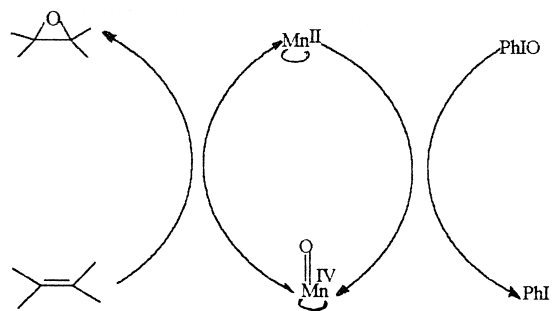

Fig. 4. Oxygen rebound mechanism.

order to find out the reason for this we irradiated the complexes with UV light and it was found that after irradiation of the UV light the spectra of the complexes undergo some change. The spectra of the irradiated complex is shown in Fig. 2. The solid precipitated during the catalytic reaction in the presence of light and PhIO was separated and the IR spectra were recorded. In this case also a clear change is observed in the spectra indicating degradation of complexes leading to reduction or inhibition in their catalytic activity.

Hence, in the case of the catalyst complexes under study, in the presence of light, the epoxidation is mainly due to the catalytic effect of light as the metal complex undergoes photodegradation. Thus, the advantages of a joint catalytic effect of both complex and light is lost as observed in the case of stable complexes, studied earlier [32], which do not undergo degradation in the presence of light.

Acknowledgements

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