Letter

Study of effect of substitution on ligands on the catalytic activity of ternary complexes

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Abstract

The ternary complexes of Fe(III) and Mn(II) with one bipyridyl or *ortho*pnenanthroline and another newly synthesised tridentate mannich base of phenyl alanine and bromo salicylaldehyde, have been prepared and characterized by elemental analyses, spectral and electrochemical studies. These complexes were used as catalysts for the oxidation of the olefines, using PhlO as the oxidant. The results of the oxidation reactions were compared with that, using unsubstituted ligand complexes as catalysts. It has also been found that the present complexes are better catalysts. © 2000 Elsevier Science B.V. All rights reserved.

Transition metal complexes of the type $(M^{n+}LA)$ are being used extensively as oxygenation catalysts, using iodosylbenzene as the oxidant [1,2]. Reaction proceeds through the intermediate formation of $LM^{n+2} = O$. The catalytic activity depends on the ease with which the oxygen is transferred by $LM^{n+2} = O$ to the substrate.

Ternary complexes of Mn(II) and Fe(III) with reduced schiff bases obtained by the condensation of salicylaldehyde with aminoacids, as one ligand and bipyridyl or *ortho*phenanthroline as the second ligand, have been synthesised earlier [3]. These ternary complexes have the advantage that the metal ion is coordinated with both σ and π donor sites, so that the electron density around the metal remains moderate. Thus the redox potential of the metal centre can be ex-

pected to be optimum so that the metal oxo species formed should be stable till it comes in contact with the substrate and transfers oxygen to it.

The substitution of electrophilic groups on the ligand reduces electron density on the metal ion, making it less electropositive. The oxo cation $Mn^{n+2} = O$ is thus rendered less stable and should transfer oxygen to the substrate easily.

To compare the catalytic activity of substituted reduced schiff base ligand complexes of Fe(III) and Mn(II) with that of unsubstituted ligand complexes, mixed ligand complexes containing one reduced schiff base ligand (obtained by the condensation of bromosalicylaldehyde and phenyl alanine) and another diimine ligand have been prepared and characterised by spectral electrochemical and mass spectral studies. These complexes were used as catalysts for the epoxidation of norboronene and *cis* cyclooctene

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and the catalytic activity has been compared with that of the analogous ternary complexes of Fe(III) and Mn(II) containing reduced unsubstituted schiff base ligand studied earlier [3].

1. Experimental

Substrates norbornene, *cis* cyclooctene and oxidation products norboronene oxide and *cis* cyclooctene oxide were obtained from Aldrich. Bromosalicylaldehyde and phenyl alanine (SRL), $MnCl_2 2H_2O$, $FeCl_3$ anhydrous (SD Fine) used were of AR grade. PhIO has been prepared by the method reported earlier [4]. Tridentate ligands were prepared by using similar methods, as reported for the unsubstituted ligands [5]. Bipyridyl and 1,10-phenanthroline (Qualigens) were used as received (Fig. 1).

Carbon and hydrogen analyses of the complexes were carried out using a Coleman analyser model −33 while nitrogen was estimated by Dumas method. Fe and Mn were estimated gravimetrically. The IR spectra were recorded on Nicolet FTIR. Electronic spectra were recorded on Shimadzu UV visible spectrophotometer UV 240. The magnetic measurements were carried out by using Gouys balance at room temperature.

The electrochemical unit used consists of model 174 A polarographic analyser, universal programmer, X–Y recorder, Pt 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 as the FAB gas and *m*-nitrobenzyl alcohol as the matrix.
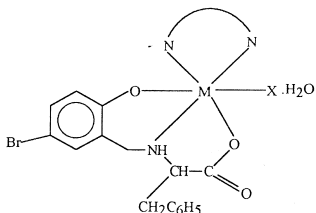
The gas chromatographic analyses were carried out on a Shimadzu GC 14B instrument equipped with oracle 3 computing integrator using 10% SE 30 with 1% QF on a chromosorb column (2 M) and nitrogen as carrier gas.

2. Syntheses of LFeACl H_2O complexes

One millimole of the mannich base ligand (L) and 2 mmoles of lithium were dissolved in 20 ml methanol and to this was added 1 mmole of $FeCl_3$ in 15 ml methanol, then the reaction mixture was stirred for about 1 h. To this 1 mmole of diimine (bipyridyl or *ortho*phenanthroline) (A) was added. The reaction mixture was stirred for about 1 h and the solid formed was filtered and washed with methanol and dried in vacuo.

3. Syntheses of LMnAH$_2$O complexes

One millimole of $MnCl_2 2H_2O$ was taken in 50 ml of 1:1 water–alcohol mixture and to this was added 1 mmole of diimine (bipyridyl or phenanthroline) in 15 ml alcohol–water (1:1 mixture). The reaction mixture was stirred for 1 h. To this was added 1 mmole of mannich base ligand and 2 mmole of NaOH in 30 ml 1:1 alcohol–water mixture. The reaction mixture was stirred for about 1 h and the solid formed was filtered, first washed with 1:1 water–alcohol mixture and then with ether and dried in vaccuo.

4. Procedure for catalytic oxidation reaction

All the reactions were carried out in a Schlenk tube under nitrogen atmosphere. The solvents used for the catalysts were water–acetonitrile (1:3 v/v) for Fe (III) complexes and acetonitrile for Mn(II) complexes. To this solution was

Fig. 1. N‿N = 1,10-Phen or Bpy; M = Fe(III) or Mn(II); X = Cl for Fe(III) complexes; X = H_2O for Mn(II) complexes.

added the substrate followed by the internal standard chlorobenzene and then nitrogen was bubbled through the solution for 10 min. The oxidant PhIO was added to this homogeneous solution. The reaction mixture was stirred at ambient temperature for about 5 h in nitrogen atmosphere. Aliquots (1 μl) were withdrawn from the reaction mixture and analysed by gas chromatograph.

5. Results and discussion

The electronic spectra of Fe(III) complexes show a band at 500 nm due to d–d transition. In the Mn(II) complexes d–d transition bands are not observed in dilute solution. A band at 400 nm may be due to charge transfer transition from phenolate O- to Mn(II).

The IR spectra of the complexes show band at 1580 and 1470 cm^{-1} indicating coordinated carboxylate group of mannich base. The NH band occurs at 3200 cm^{-1} indicating coordinated NH group in the complexes. A broad band is observed in the complexes 1 and 2 in the region 3300–3500 cm^{-1} due to water molecule in the complexes.

The magnetic susceptibility measurements at room temperature shows that Mn(II) and Fe(III) complexes are high spin paramagnetic compounds and the magnetic moments, between 5.5 and 6.3, correspond to five unpaired electrons (Table 1).

The cyclic voltammetric studies of Fe(III) complexes were carried out in acetonitrile water medium. Two reduction peaks were obtained

Table 1
Analytical and magnetic moment data of the complexes

Complexes	Analysis[a]				μ_{eff}
	C	H	N	M	
I	51.1(50.9)	3.9(3.8)	6.8(6.9)	8.6(9.1)	6.4
II	52.7(52.7)	3.8(3.6)	6.6(6.6)	8.8(8.8)	6.1
III	54.1(54.2)	4.2(4.0)	7.3(7.3)	9.9(9.5)	
IV	55.7(56.0)	4.0(3.8)	6.9(7.0)	8.7(9.2)	5.4

[a]Calculated values in parentheses.

Table 2
Results of epoxidation
Substrate:oxidant:catalyst mole ratio 250:50:1.
Solvent H_2O:CH_3CN (1:3 v/v) for complexes 1, 2 and CH_3CN for complexes 4,5.

Olefins	Product	Yield[a] with catalyst			
		1	2	3	4
Norbornene	Norborene oxide	4	5	46	–
Cyclooctene	Cyclooctene oxide	9	5	65	56

[a]Yield base on iodosyl benzene discharged.

for both the complexes assignable to Fe(III) → Fe(II) → Fe(I) reductions. In both these cases the electrochemical reactions are completely irreversible.

In the FAB mass spectra of the complex 1, the peak at $m/z = 595$ corresponds to the parent ion. Other peaks obtained correspond to LFeCl at $m/z = 405$, AFeCl at $m/z = 247$ and AFe at $m/z = 213$. For manganese complex 4, peaks were obtained at $m/z = 583$ corresponding to the parent ion. Peak at $m/z = 399$ corresponds to LMn, at $m/z = 253$ to $MnAH_2O$ and at $m/z = 235$ to MnA.

6. Catalytic reactions

The results of the oxidation of olefins with PhIO in the presence of all complexes are shown in Table 2.

The yield of the oxygenated product is much more in the case of Mn(II) complex catalyst than in the case of corresponding Fe(III) complex catalysts.

To suggest the mechanism of oxidation reaction, UV visible spectra of the complexes were recorded in the presence of PhIO. The colour of the Fe(III) complexes change from violet to reddish, and in the visible spectrum original d–d band of the complex shifts its position to 480 nm. This can be attributed to the formation of metal oxo species.

In the presence of PhIO, Mn(II) complex solutions turned dark brown and a new peak

was observed at 510 nm. This may be due to the formation of $Mn^{IV} = O$ as suggested earlier [6].

The electrochemical studies were carried out in the presence of PhlO. On addition of PhlO to the Fe(III) complexes, the two reduction peaks completely disappeared and a new response occurred at less negative potential. This can be attributed to Fe(V) to Fe(IV) reduction, supporting the formation of Fe(V) = O on addition of PhlO.

The oxygen transfer takes place through the formation of $M^{n+2} = O$. The termination of the reaction is because of the degradation of the complexes, as there is no spectral evidence for the formation of the μ oxo species. It was observed earlier that mannich base complexes are more susceptible to oxidative degradation [7].

It can thus be concluded that Mn(II) complexes are catalytically more active than the corresponding Fe(III) complexes. It has also been clearly seen that the bromine substitution in the aromatic part of the tridentate ligand increases the catalytic activity of the complexes. A similar observation was made earlier [8,9] in the case of tetradentate ligand complexes.

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