CHAPTER 5
Macrocyclic ligand complexes

Studies of synthetic models mimicking cyt P-450 fall into two broad categories, namely, those involving metal porphyrins[1] and those involving non-porphyrinic complexes[2]. Non-porphyrinic complexes used are mainly of open ligands, though a macrocyclic ligand complex is a closer model to cyt P-450 Very few studies have been devoted to non-porphyrinic macro-cyclic ligand complex models, except some recent reports of oxidation studies using iron(II), iron(III), ruthenium(II), ruthenium(III), cobalt(II) and nickel(II) cyclams and related complexes [3-7]

This chapter describes synthesis of hexa-aza macrocyclic ligand by condensation of 2,3-butanedione with aliphatic amine- diethylenetriamine - and preparation of complexes of manganese(III), iron(III) and cobalt(III) with the macrocyclic ligand. The complexes have been characterized and used as catalysts for epoxidation of olefins

Experimental

2,3-Butanedione (Merck), diethylenetriamine, sodium tetraphenylborate, sodium perchlorate, tetrabutylammonium iodide and iodobenzene (Fluka) were used as received. All other reagents used were of AR grade Methanol for synthesis was super dried [8] and stored over 4A molecular sieves. Other experimental conditions were same as described in the preceding chapters.

Synthesis of complexes

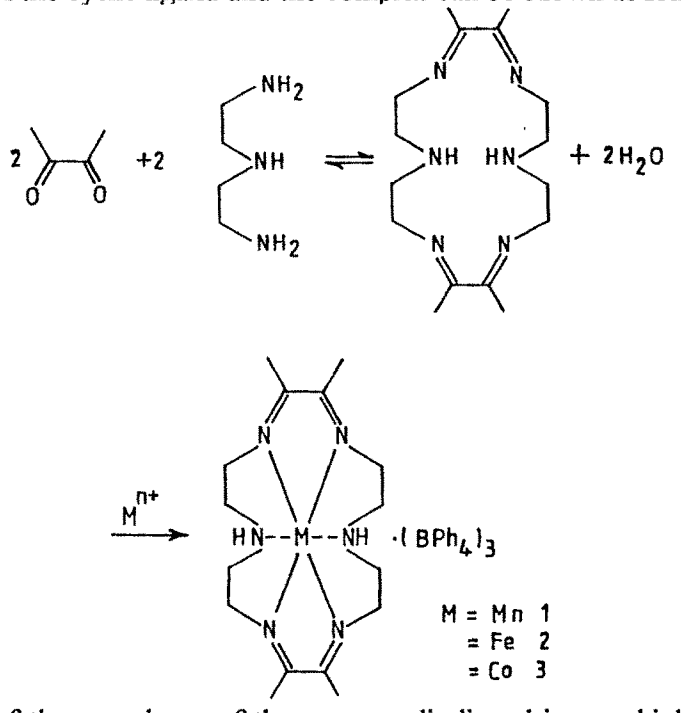
The general procedure followed for the synthesis of the complexes 1-3 is given below Super dry methanol was used for all syntheses

To a 50 ml methanol solution containing 1.22 x 10^{-3} M of amine was added dropwise, 50 ml methanol solution of 1.2 x 10^{-3} M 2,3-butanedione, with vigorous stirring. The solution was then refluxed for 30 min, whereupon it turned yellow. Refluxing was stopped and to the warm ligand solution, 20 ml methanol solution of metal salt (1.2 x 10^{-3} M) ($MnCl_2.4H_2O$, $FeCl_3$, $CoCl_2.4H_2O$) was added dropwise with stirring and then the reaction mixture was refluxed for 25 h. The resulting dark solution was cooled and 3.7 x 10^{-6} M of $NaBPh_4$ salt was added to it. The dark complex thus precipitated was suction filtered, washed with a minimum volume of cold, dry, methanol and vacuum dried at room temperature.

Epoxidation Studies : The method and the apparatus used were same as described in the previous chapters. The complex 1 was used as catalyst for the epoxidation of Norbornene, cyclohexene, styrene and *cis*-cyclooctene For comparison, complexes 2 and 3 were also used as catalysts for the epoxidation of *cis*-cyclooctene.

Results and Discussion

High dilution method has been used in the synthesis of the macrocyclic ligands to avoid polymerization. The metal complex is formed on addition of metal salt to the ligand solution in-situ. Formation of the cyclic ligand and the complex can be shown as follows.



Solubility of the complexes of the macrocyclic ligand is very high in methanol and a large counter ion, BPh_4^-, is required to precipitate them.

Table 1 shows elemental analyses for these complexes, which correspond to the expected formulae. Complexes 1-3 are expected to be distorted octahedra, with two >NH on axial sites. IR spectra for all the complexes were broadly similar. They showed absence of $-NH_2$ and >C=O stretching vibrations in the region 3200 cm^{-1} and 1700 cm^{-1} respectively, indicating formation of macrocycles. Strong bands in the region of 1645 - 1625 cm^{-1} confirm presence of imine linkages. Magnetic susceptibility values for the complexes correspond to their oxidation state +3 (Table 1).

All the complexes **1-3** act as weak catalysts for epoxidation of olefins (Table 2) This may be because the complexes are hexacoordinate and coordinatively saturated and hence are expected to be poor epoxidation catalysts due to non availability of vacant sites for reaction The weak catalytic activity may be because the two axial nitrogens are weakly bound to metal ion and can easily be displaced either by solvent or by the oxidant In case of *cis*-cyclooctene epoxidation, the change of metal ion in the complex catalyst does not significantly change the yield of epoxide.

Electronic spectral and electrochemical potentials were studied to suggest the mechanism of the reaction. Complex **3** does not show any characteristic absorption in acetonitrile from 300-700 nm **1** and **2** both show absorptions at 364 nm. Addition of PhIO to the solution of **1-3** does not generate any new absorption band and the original absorptions remain intact, showing that oxo cation is probably not formed on addition of PhIO

Cyclic voltammetry of the complexes **1-3** in water-dioxane (1:1 v/v) does not show any clear discernible feature Complexes **1-3** show no redox peak in the 1st cathodic cycle from 0.00 V to -1 00 V. In the anodic run from -1 00 V to +1 00 V, a diffused redox peak is seen at +0 62 V, for which corresponding reduction wave is not observed Complexes **1-3** show similar behaviour in DMF solvent In first sweep from 0 00 to -1 00 V, no cathodic peak is seen, and on sweeping from -1 00 to +0 70 V, a clear anodic peak at +0.56 V is observed, for which, the corresponding reduction peak at +0 50 V is not well resolved This redox couple shifts with scan rate Addition of PhIO does not bring in any change in the voltammograms Since the values of the redox behaviour are same for all the complexes, a probable assignment could be ligand based oxidation rather than metal centered oxidation

These observations suggest that in the complexes, change in the oxidation state of the metal ion is not facile.

UV-vis measurements and CV studies show that reaction of the complexes with PhIO does not generate the high-valent metal-oxo species, required for the 'oxygen rebound' mechanism of epoxidation as followed by the cyt P-450 mimics[9] and other complexes studied earlier. The present macrocyclic ligand complexes gave limited epoxidation yields probably by the lewis-acid catalysis, as suggested by Valentine[10], which does not require formation of the high-valent metal-oxo species. This mechanism also explains comparable epoxide yields obtained with all the three complexes containing different metal ions. Further support for the pathway is the observation that epoxide yields vary with type of olefin. Tentatively, the difference in the catalytic activity and pathway of epoxidation reaction of the open chain schiff base complexes studied earlier [11] (oxygen rebound mechanism) and the macrocyclic schiff base ligand complexes studied in the present investigation (Lewis-acid mechanism) can be attributed to the constraint imposed by the hexadentate macrocyclic ligand

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Table 1 Elemental analysis and magnetic moments for complexes **1-3**

Analysis (Th) %	**1**	**2**	**3**
C	79.4 (80 1)	81.0 (80 1)	79.2 (79.9)
H	6.5 (6.9)	6.2 (6.9)	6.4 (6.9)
N	6.9 (6 4)	6 7 (6 4)	6.8 (6 4)
μ_{eff} B M	4.81	3 76	4.72

Table 2 - Complexes **1-3** as epoxidation catalysts[a]

Substrate	Complex	Epoxide Yield %(PhIO based)
Norbornene	**1**	10
Cyclohexene	**1**	6(22[b],11[c])
Styrene	**1**	3
cis-Cyclooctene	**1**	7
cis-Cyclooctene	**2**	8
cis-Cyclooctene	**3**	6

a Cat : PhIO : Olefin mole ratio = 1:50:250, cat = 0.01 mmole

b cyclohex-2-en-1-one

c cyclohex-2-en-1-ol