SUMMARY AND CONCLUSIONS

The theme of the present investigation is mainly concentrated on the synthesis, characterization and catalytic activity studies of some zeolite encapsulated transition metal complexes. Synthesis of a series of Y zeolite encapsulated chiral transition metal complexes, their characterisation and efficiency as catalysts in inducing chirality in the epoxidation of a prochiral olefin was investigated. The characterization studies were mainly based on the XRD studies to check the crystallinity, surface area determinations to know the extent of encapsulation, and magnetic and spectral studies to confirm the complexation. The catalytic efficiency with respect to oxidation activity, recyclability and stability of the catalytic system were examined. Chapter I is an introductory chapter that presents a general discussion on zeolite encapsulated metal complex systems and the catalytic studies reported based on such systems. This chapter also provides a brief account of various methodologies for the synthesis of zeolite complexes. The scope of the present investigation is also presented in this chapter.

Chapter II gives the general procedures for the synthesis of the Y zeolite encapsulated complexes, the details of reagents and materials used, and the characterization techniques employed. The techniques used in the present study include chemical analysis, CHN analysis, TG, GC, ICP, XRD, SEM, BET surface area and magnetic moment measurements, diffuse reflectance, FTIR and EPR spectrometry.

Studies on the synthesis and characterization of Y zeolite encapsulated Mn(II), Co(II), Ni(II) and Cu(II) complexes of some Schiff base ligands are presented in chapters III, IV, V, and VI. Chapter III deals with the results of our studies on the complexes of the ligand, N,N'-bis(salicylidine)-1,2-
phenylenediamine (SOPY). The zeolite NaY used for supporting the complexes was found to possess a unit cell of formula Na$_{56}$[(AlO$_2$)$_{36}$(SiO$_2$)$_{36}$].xH$_2$O. The unit cell formulae of metal exchanged zeolites were also derived from the analytical data. The Si/Al ratio of metal exchanged zeolites is found to be approximately in the range 2.3 – 2.4 and it is almost near to that of the parent zeolite indicating that there is no collapse of the zeolite framework. It was prevented in the present study by the use of dilute metal salt solutions. Surface area, XRD and FTIR data of metal exchanged zeolites also reveal the retention of zeolite framework.

The empirical formulae of the zeolite encapsulated SOPY complexes could be obtained from the analytical data. SE micrographs of the encapsulated complexes, before and after soxhlet extraction, indicate that surface adsorbed complexes are absent. XRD patterns and Si/Al ratio indicate the retention of zeolite framework on encapsulation. The lower surface area of encapsulated complexes as compared to those of the corresponding metal exchanged zeolites suggest encapsulation of the complexes within the zeolite pores.

The geometry of the Mn(II) complex is assigned to be octahedral from the spectral and magnetic studies. The complex also gives EPR spectrum characteristic of I = 5/2 systems. From the spectral and magnetic studies, the Co(II) and Ni(II) complexes are assigned a tetrahedral and distorted tetrahedral geometries respectively. The zeolite Y encapsulated Co(II)SOPY complex is also found to be EPR active and its EPR indicates Co(II) ion in the high spin state. The electronic spectrum and the magnetic moment value suggests a tetragonal geometry for CuSOPY. EPR spectrum indicates an axial symmetry for CuSOPY. It also reveals the ionic nature of the metal ligand bonding in this complex.

The formation of the complexes in the zeolite pores was also confirmed from the IR data. The $\nu$(C=N) bond of the Saloph ligand, which is found to undergo a blue shift in all the complexes. Such a blue shift of the band is also reported earlier for zeolite encapsulated complexes. The TG patterns of the encapsulated complexes indicate two stages of decomposition. The approximate stability of the
complexes could be ascertained in most of the cases. However, due to the small concentration of the complex in the zeolite no quantitative inferences could be drawn from the TG data.

Chapter IV presents our studies on the zeolite encapsulated transition metal complexes of the \( \text{N,N}'\text{-bis}(2\text{-hydroxymethylbenzyledine})\text{-1,2-phenylenediamine} \) (OHOPY). Surface area and XRD studies provide strong evidence for the encapsulation of the complex without the loss of crystallinity. Based on magnetic moment, electronic and EPR spectral data, the encapsulated Mn(II), Co(II), Ni(II) and Cu(II) complexes are expected to have an octahedral, tetrahedral, distorted tetrahedral and tetragonal geometries respectively. IR spectra confirm the formation of complexes in the zeolite cages and indicate the coordination of the ligand. TG patterns of the all complexes are similar and show two stages of decomposition.

Chapter V describes our studies on the zeolite Y encapsulated transition metal complexes of the ligand \( \text{N,N}'\text{-bis}(2\text{-pyridinemethylene})\text{-1,2-diaminoethane} \) (M2PyEnY). The diffuse reflectance spectra and the magnetic susceptibilities suggests an octahedral geometry for the Mn(II) complex, a tetrahedral and distorted tetrahedral symmetry for Co(II) and Ni(II) complexes and a tetragonal geometry for the Cu(II) complex. The EPR spectrum shows axial symmetry for the encapsulated Cu(II) complexes. TG data indicates the formation of complexes in zeolites.

Chapter VI deals with the studies on the encapsulated complexes of \( \text{N,N}'\text{-bis}(3\text{-pyridinemethylene})\text{-1,2-diaminoethane} \). The Mn(II) complex is octahedral. A tetrahedral structure is assigned for Co(II) and Ni(II) complexes. The Cu(II) complex has a tetragonal symmetry around the metal ion. The structural features are concordant with the EPR spectral data obtained. T.G. analysis data of these complexes is also provided in this chapter.
Chapter VII describes our studies on the catalytic activity of the Y zeolite encapsulated Schiff base complexes. All the Mn(II) complexes catalyse the oxidation of ascorbic acid among which Mn(SOPY) is found to be the least active complex and MnOHOPY has highest activity. Mn2PyEnY and Mn3PyEnY also show good activity. All the Co(II) complexes are highly active in the oxidation of ascorbic acid. The Ni(III) complexes are found to be considerably active in the oxidation of ascorbic acid. The involvement of a Ni(III) species as an intermediate may be the reason for this interesting observation. All the Cu(II) complexes are also active in the oxidation of ascorbic acid. The activity of Cu2PyEnY and Cu3PyEnY complexes are substantially higher, which may be due to the formation of a Cu(I)-substrate intermediate. All the complexes are found to be good catalyst precursors rather than good catalysts.

Chapter VIII deals with our studies on the zeolite Y encapsulated chiral transition metal complexes. Their structures arrived from the electronic spectral and magnetic moment studies are octahedral for Mn(II) and square planar for Co(II), Ni(II) and Cu(II) complexes. The complexation of the ligand is confirmed from the IR Spectra. The XRD and surface area measurements reveal the formation of the complex within the zeolite framework keeping its crystallinity. The catalytic efficiency and effectiveness in inducing chirality of the complexes were examined in the epoxidation of styrene, which is a terminal prochiral olefin. Catalysis using many oxidizing agents was investigated. We could get substantial yield of the epoxide with 3-chloroperoxybenzoic acid as the oxidant. A number of unwanted side-products were formed with all other oxidants. The enantiomeric excesses were calculated for the products obtained with 3-chloroperoxybenzoic acid. The Ni(II) complex was found to be highly enantioselective (ee = more than 98 %). The enantiomeric excess (ee) was found to be moderate for the Cu(II) complex. The Mn(II) and Co(II) complexes were giving only negligible enantiomeric excesses.
The general conclusions drawn from these studies are as follows

1. Transition metal complexes were successfully encaged within the Y zeolite framework by carefully synthesizing the metal exchanged zeolites and zeolite complexes at optimized conditions.

2. The use of zeolite encapsulated complexes as catalysts provide information regarding the advantages of heterogenisation of the homogeneous catalytic systems by the encapsulation. The encapsulated complexes prepared exhibited higher stability, better catalytic activity and recyclability in certain reactions by retarding the deactivation processes.

3. Zeolite encapsulated complexes were found to be active in the oxidation of ascorbic acid to dehydroascorbic acid. The Cu(II) complexes were the most active catalysts. Interestingly, the Ni(II) complex was also found to be highly active. This may be due to the formation of a Ni(II) species as intermediate, which is stabilized by the electronic field present within the cage.

4. The geometry of the encapsulated complexes plays a vital role in regulating the functioning of the catalyst by providing vacant reaction sites. Encapsulated complexes interact with the framework of the zeolite, thus distorting the geometry resulting in modified catalytic activity. Hence, the activity and poison resistance of these catalysts can be optimised by varying the stereochemistry with bulkier ligands.

5. The successful encapsulation of chiral SALEN type metal complexes within Y zeolite has been achieved and the enantio-selectivity of the catalysts in the epoxidation of styrene was observed. The Ni(II) complex was found to give very high enantiomeric excess.