CHAPTER-X
CONCLUSIONS

The present thesis contains EPR studies on a number of binuclear complexes, such as copper-copper, copper-zinc, nickel-nickel in addition to paramagnetically doped metal systems. In addition to EPR, various spectroscopic techniques such as UV-Vis, IR, NMR, X-ray, cyclic voltammetry and magnetic studies have been undertaken, wherever possible. The ligand has been chosen due to its importance in various types of binding to metal ions. In the first complex, the copper-copper dimer has shown interesting EPR results with half field transition and allowed to measure the D values. Also, strong half field transition is observed around 140 mT, having seven hyperfine lines (hyperfine value = 6.1 mT) from the two interacting copper nuclei. In addition, single crystal X-ray studies on this system has indicated that the two metal centers are in different geometries and the distance between them is appropriate for metal-metal interaction. The notable feature of the structure is that the Schiff base acts as a bidentate ligand (phenolic O- and imine -N=) with one of the copper ion and hetero nitrogen atom coordinating with another copper ion. Single crystal studies on the system are necessary to completely understand the interaction between the metal ions.

Yet another copper-copper complex has been synthesized, which has no acetate bridging. Single crystal EPR studies confirm the orthorhombicity of the g tensor, with appreciable D and E values. Interesting observation is the presence of a highly intense triplet spectrum with large D and high g anisotropy. The resonances due to this set are noticed only in one crystal plane of rotation, whereas in other two planes, the low field lines are only present. The large g value noticed for this set indicates very low lying exciting states with a strong interaction with the ground state. In addition, the observation of seven line pattern at parallel component indicates a weak coupling of copper ions in the system. Half field transitions are not noticed even for solution spectrum at low temperatures. This multi behaviour of the dimers in the complex needs further investigation at Q-band frequencies.

Two more copper-copper and copper-zinc complexes have been synthesized. These complexes have μ-1,1-azido bridging. The powder EPR spectrum of copper-copper complex at room temperature and at 77 K confirms the presence of two copper ions, which are interacting. However, the half-field transition does not show any superhyperfine lines due to the dipolar broadening. The solution spectrum at 77 K clearly shows the presence of 7
superhyperfine lines from the two interacting copper nuclei. On the other side, the Cu-Zn complex further confirms the dicopper complex results with one zinc ion and has behaved in an expected manner. Single crystal work on these systems will be very interesting with magnetic data below 77 K.

The synthesis of a binuclear Nickel(II) complex is achieved. The two nickel ions are joined by perchlorate bridging. Interestingly, the EPR data is observable even at room temperatures, making it one of the very few systems giving rise to EPR resonances at room temperature. The spin Hamiltonian parameters have been calculated from single crystal data. The distortion is small and the interaction between the two nickel centres is also very weak. The EPR data has been collaborated with optical data to obtain Dq and Racah parameters. Further work at Q-band frequencies and single crystal X-ray work will help to understand the system in a more detailed way.

Systematic analysis of the EPR spectra of VO(II) doped Lithium potassium sulphate lattice (LKS) has been undertaken to study the effect of the ion on phase transition. LKS has a number of phase transitions in the entire temperature range. The EPR spectra are complicated due to the presence of more than one paramagnetic site in the lattice. We have identified four such sites and the spin Hamiltonian parameters are calculated for all the sites with the help of the powder spectrum and single crystal rotations. The powder spectrum also clearly shows three different sites. However, due to slight deviation from axial symmetry, it is not shown up in the powder spectrum. An important and exciting observation is the absence of phase transition, down to 77 K. This has been confirmed by recording the powder spectrum from 300 to 77 K. We do not notice any splitting or collapse of lines during the temperature change. As far as we know, this is the first case of a phase transition disappearance when a paramagnetic ion is introduced. However, further work at Q-band and low temperature (below 77 K) is a must to fully substantiate our results.

EPR studies of Cu(II) in ZAPH are reported over a wide temperature range from room temperature to liquid nitrogen temperature. The temperature dependence of EPR spectra and spin Hamiltonian parameters have shown that the coordination polyhedron around the host Zn(II) ion corresponds to a tetragonally compressed octahedron of oxygen atoms of water. However, when Cu(II) is doped, the axially symmetric room temperature EPR spectrum has "pseudo g_o>pseudo g_1", indicating a dz^2 ground state. However, the low
temperature and variable temperature spectra clearly indicate that the room temperature spectrum is a thermal averaged one and hence is a $dx^2-y^2$ ground state. The $g$ and $A$ tensor direction cosines match fairly well with Zn-O directions, confirming that Cu(II) enters the lattice in place of Zn(II). It is also interesting to note that the direction cosines of $g$ and $A$ tensors remain unaltered from 300 to 77 K. Various Jahn Teller parameters such as related populations in the two lowest JT valleys, JT stabilization energy, strain coefficient etc. have been calculated.