The thesis entitled "EPR STUDIES ON PURE BIMETALLIC AND DOPED MONOMETALLIC COMPLEXES" deals with the preparation and characterization of a Schiff base ligand and its homobinuclear metal complexes of copper (with different bridging moieties); heterobinuclear complex of copper and zinc and nickel with various spectroscopic techniques, along with single crystal EPR studies on a vanadyl ion incorporated into lithium potassium sulphate (LKS) and a copper ion substituted in zinc potassium phosphate hexahydrate (ZPPH). The thesis consists of ten chapters, including the conclusion section. The brief contents of the various chapters are described below.

Chapter I deals with the literature survey on homo and hetero bi and multinuclear copper complexes with various types of Schiff base ligands and an introduction to the theory and basic principles of EPR spectroscopy. In addition, a brief review on EPR studies of Cu(II) and VO(II) ions doped in various host lattices are also presented. Chapter II begins with an outline of the experimental details of EPR spectroscopy and other types of technical details. Chapter III presents the preparation and characterization of the Schiff's base ligand, 2-[(4-Methyl-pyridin-2-ylimino)-methyl]-phenol (abbreviated as Hsalamp), by elemental analysis, IR, UV-Vis, NMR and mass techniques.

Chapter IV describes the preparation and characterization of a dimeric copper complex with ligand Hsalamp. The complex is prepared by adding an methanolic solution of one equivalent of ligand with a solution of one equivalent of copper acetate and one equivalent of lithium perchlorate, both dissolved in pure dry methanol. The complex has been characterized by elemental analysis, UV-visible, IR, X-ray, dp, conductivity and EPR techniques. The UV-Visible spectrum shows absorption bands at 672, 397, 288 and 235 nm. The first one pertains to d-d band, while the rest are due to charge transfer. The IR spectrum reveals a band at 1095 cm⁻¹, indicating the presence of uncoordinated perchlorate ions. The other band at 1610 cm⁻¹ reveal C=N stretching. The EPR spectra are recorded for the powder and solution samples at room temperature and 77 K. The EPR spectra of powder sample at RT and 77 K is that it represents a typical
triplet spectrum, with g values of 2.25, 2.15 and with zero field splitting parameter close to 113 mT. In these cases, we do not observe half-field transitions, as expected for a dimer. The sample has given an isotropic EPR spectrum in methanol solvent at RT. On cooling the solution sample to 77 K, an EPR spectrum having g values 2.13, 2.07 and 2.05 and with D values 77.5, 44.6 and 1.6 mT is obtained. In addition to this, a strong half field transition is observed around 110 mT, having seven hyperfine lines (hyperfine value = 6.1 mT) from the two interacting copper nuclei. This dimeric nature has also been confirmed by X-ray analysis. The crystal structural data collected at 293 K reveal that the copper complex contains two types of copper ions, with one of them having a penta-coordination, while the other is four-coordinated. The XRD data is: Triclinic, Point group = P-1, a = 0.89532, b = 1.27423, c = 1.49012 nm, α = 73.77, β = 75.32, γ = 77.50 and Z = 2. 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. The magnetic susceptibility data recorded as a function of temperature at 15 different temperatures reveal a weak ferromagnetic property. The cyclic voltametry and dp studies also point to a one-step two electron transfer, which indicates the reduction of the two copper ions to copper.

Chapter V describes the synthesis and characterization of yet another dicopper complex with the same ligand. This complex has been prepared by taking two equivalents of the ligand with two equivalents of copper perchlorate in dry methanol. The UV-Visible spectrum shows a characteristic absorption at 684 nm pertains to d-d band. The bands at 384, 275 and 235 nm have been attributed to charge transfer. In addition, the conductivity measurements reveal that the complex is 1:2 electrolyte. The IR spectrum reveals characteristic bands. The magnetic susceptibility data reveals a weak ferromagnetic property. The dp study is indicative of a one step, two electron transfer, confirming the reduction of the two copper ions to copper. Crystal rotations have been done in three orthogonal planes and the three road maps have been used to get g and D-matrices with the help of computer program. The powder and solution spectra have been recorded at RT and LNT. The spin Hamiltonian parameters obtained from powder matched with single crystal data. An interesting observation in the frozen solution is that the low field side of zero-field splitting line splits into seven lines. Here,
the half-field transition resonance is very low in intensity, due to the absence of acetate bridge makes the two copper ions to increase their distance.

Chapter VI describes the preparation and characterization of two more bimetallic complexes with the ligand Hsalamp. Copper-copper complex has been prepared by mixing methanolic solutions of ligand, copper perchlorate and sodium azide. The UV-visible spectra show a d-d absorption band at 671 nm and charge transfer bands at 394 nm, 289 nm and 235 nm. The IR band at 1094 cm\(^{-1}\) indicates the presence of perchlorate ions. The other band at 1610 cm\(^{-1}\) reveal C=N stretching. Absorption at 2076 cm\(^{-1}\) confirms the presence of azide linkage. The magnetic susceptibility data indicate a weak ferro magnetic property. The EPR powder data at RT shows a peak at \(g = 2.17\) and its solution at RT has \(g_{iso} = 2.16\) and \(A_{iso} = 5.11\) mT. This agreement between powder and solution indicates no structural changes. The corresponding data at 77 K is 2.17; 2.07, 2.13 and 2.04 (no A values). The D values have also been calculated. Here also, we observed half field transition with a well resolved 7 hyperfine lines, indicating the dimeric nature of the complex. The EPR spectra have been simulated.

The copper-zinc complex has been prepared by mixing methanolic solutions of ligand, zinc perchlorate, copper perchlorate and sodium azide. This complex is also a dimer, however, having one copper and one zinc, as evidenced from our EPR results. The UV-Visible spectra show a d-d absorption band at 657 nm and charge transfer bands at 395, 281 and 239 nm. The IR band at 1098 cm\(^{-1}\) indicates the presence of perchlorate ions. The other band at 1606 cm\(^{-1}\) reveal C=N stretching. Absorption at 2072 cm\(^{-1}\) confirms the presence of azide linkage. The conductivity measurements reveal that the complex is 1:1 electrolyte. The EPR results indicate a typical mono-copper with a small dimer (copper-copper) impurity. The repeated experiments to remove the dimer component are not successful. The powder spectra at RT and LNT indicate a single g value close to 2.18. The solution RT has g value of 2.14 and Aiso of 5.76, slightly higher than the dimer value. The LNT solution spectrum indicates the monomer along with the dimer impurity. The g values are 2.14 and 2.05 and A values are 6.48 and 2.6 mT. However, the low A values indicate the transfer of spin density on to the ligands.
Chapter VII presents the synthesis and characterization of a dinickel complex with the ligand Hsalamp. This complex has been prepared by taking two equivalents of the ligand with two equivalents of nickel perchlorate in dry methanol. The conductivity measurements reveal that the copper complex is 1:2 electrolyte. The UV-Visible spectra show three strong absorption d-d bands at 441, 660 and 998 nm. A weak absorption at 741 nm corresponds to spin-forbidden transition. The IR band at 1094 cm$^{-1}$ indicates the presence of uncoordinated perchlorate ions. The other band at 1608 cm$^{-1}$ indicates C=N stretching. The complex gave a well-resolved EPR spectrum at room temperature, even though it is a d$^8$ system. Single crystal rotations are performed in the three orthogonal planes and the data has been analysed. The results indicate that the complex has very low distortion, indicated by the low value of zero-field splitting. The g and D matrices have been analysed and compared with the x-ray data of Complex-I. The EPR results further indicate that the two nickel ions present in the complex are not interacting appreciably to give complicated and broadened spectra. However, at few places, we can notice two different types of nickel ions. From the optical data, the Dq and Racah parameters have been calculated, from which the covalency of the metal-ligand bond has been estimated.

Chapter VIII describes the single crystal EPR results of VO(II) doped in Lithium Potassium Sulphate, LiKSO$_4$ (LKS). As the host lattice has been studied earlier for phase transition identification, an attempt has been made to understand the effect of dopant on phase transition temperature, and then study the behaviour of the vanadyl ion. Hence, single crystal rotations are done at room temperature in the three mutually orthogonal axes to obtain spin Hamiltonian parameters. Due to charge compensating effect (+2 ion can substitute for monovalent Li or K), a number of sites for VO(II) ion in the lattice have been noticed. However, analysis has been made only for four sites. The intensity of the other sites is relatively weak to follow them completely throughout the crystal orientation. The spin Hamiltonian parameters calculated from the iso-frequency plots are: $g_{||} = 1.9459$, $g_{\perp} = 1.9974$, $A_{||} = 19.6$ mT, $A_{\perp} = 7.4$ mT; $g_{||} = 1.9293$, $g_{\perp} = 1.9901$, $A_{||} = 20.4$ mT, $A_{\perp} = 7.5$ mT. Nearly four chemically inequivalent sites have also been noticed in the powder spectrum of VO(II)/LKS at room temperature. The 77 K EPR powder spectrum almost matches with the room temperature spectrum, indicating no phase transition during this temperature range.
Chapter IX describes the doping of Cu(II) in ZPPH host lattice. The room temperature single crystal EPR spectrum of this complex consists of unresolved hyperfine lines from copper nucleus. Cooling the sample to 77K has resulted in well-resolved spectra. Single crystal rotations have been done at 300 K, 143 K and 77 K suggest that the g and A values highly temperature dependent. In addition, the line width is also temperature dependent. The spin Hamiltonian parameters are calculated at these three temperatures. Even though, the g and A values are highly temperature dependent, whereas the direction cosines of these matrices are not. Also, as the sample is cooled, the g and A values (two out of three) have been changed, while the third one remains almost constant. These observations indicate that the system is an example of Dynamic Jahn-Teller distortion. A misleading in the ground state has been removed by measuring the powder spectrum as a function of temperature. Various Jahn Teller parameters have been calculated. The optical data has been collaborated with EPR results to get admixture coefficients.

The thesis ends with a conclusion (Chapter X) highlighting the new observations presented in the present investigation, along with future work for these systems. It is worth mentioning that the reaction conditions are very critical in obtaining the mono and/or bi (homo or hetero) metallic complexes. Single crystal studies done on the bimetallic copper complexes clearly indicate the half field transition containing the hyperfine lines from both the copper nuclei is scarcely reported in the literature. The observation of seven hyperfine lines at half field transition, arising from two copper nuclei indicate that the interaction between the two copper ions is not very high to broaden the lines or too small, not to notice seven lines. Plans are to grow single crystal suitable for EPR studies to understand the variation of these lines as a function of magnetic field. In addition, the doping of VO(II) in LKS does not show any phase transition down to 77K needs further thinking to explain this observation. We hope that this is the first time that a disappearance of phase transition, when a paramagnetic impurity is doped. Also, the behaviour of Cu(II)/ZPPH is interesting that the spin Hamiltonian parameters are highly temperature dependent, whereas the directions of the g and A tensors are temperature independent. This is also another unique observation.