In the present thesis, single crystal EPR studies of some first row transition metal ions such as Cu(II), Mn(II) and VO(II) doped in a few dia- and paramagnetic host lattices have been reported. In addition to single crystal EPR studies, optical studies are also carried out, wherever it is necessary and feasible. The main aim of the thesis is to predict the location of the paramagnetic impurity, when incorporated in nearly octahedral symmetry, having different types of ligands. For this, four lattices have been selected, out of which one of them is paramagnetic host. The four host lattices used for the single crystal EPR studies are dipotassium diaquabis(malonato-κ²O,O') zincate(II) dihydrate (PMZD), diaqua- malonatozinc(II) (DAMZ), magnesium potassium phosphate hexahydrate (MPPH) and cobalt ammonium phosphate hexahydrate (CoAPH). A total of three paramagnetic impurities viz., Cu(II)), Mn(II) and VO(II) are selected for this study. The latter two ions are doped in DAMZ lattice in order to study the bonding nature and the orientation property of the dopant in the lattice. Since polyfunctional carboxylate systems are found to be less sterically hindered in their bridging potential than o-eba, a study has been undertaken to evaluate the binding of Zn(II) by malonate ion which acts as a more attractive fortifying agent for eugenol. As mentioned earlier, since the central metal ion is six coordinated in the host lattices, it is easy to compare the effect of the paramagnetic impurity in all the lattices.
Single crystal EPR investigation of copper(II) doped in PMZD results in interstitial insertion of copper(II) in the lattice. Two positive charges (K⁺) are set free to ensure the charge neutrality of the interstitially occupying divalent copper ion. Though the crystal lattice contains two molecules per unit cell, only one site is observed for the copper ion and that too turns out to be interstitial. EPR studies on Cu(II) indicates a tetragonal distortion and this is further confirmed from the optical absorption studies. Another exclusive feature observed is the astonishingly low hyperfine value for the parallel component of copper nucleus. Such a low value is the consequence result of the admixture of dₓ²-y² and dₓ² orbitals. The admixture coefficients are calculated by iterative method and the best fit values with the spin Hamiltonian parameters are compared with the previously reported values.

As mentioned earlier EPR studies on DAMZ lattice are done by doping VO(II) and Mn(II) ions. The paramagnetic ions show similar behavior in the lattice. Only one site of the paramagnetic impurity has been identified even though crystal structure indicates four molecules per unit cell. Interestingly, both the paramagnetic ions enter the lattice interstitially. The exact location of the interstitial position, when Mn(II) is incorporated in DAMZ lattice has been identified from the X-ray data. Even though two sites are noticed, only one is followed, since the second one has a very low D value. In the single crystal EPR studies of Mn(II), the zero field term turns out to positive, after a close look at the hyperfine interaction. The covalency of the metal ligand bond is calculated as 8.5%. Since the central
metal ion is diamagnetic (Zn(II)) in this host lattice, the relaxation studies are not carried out.

Single crystal EPR studies of vanadyl ion doped in DAMZ reveals rhombic symmetry for the dopant, which is further confirmed by optical studies. Due to the strong directional dependence of V=O bond, the exact location of the impurity could not be located. However, the general spin Hamiltonian parameters behaved in a normal manner. The Fermi contact parameter (κ) and dipolar interaction parameter (P) have also been calculated and the covalency of the metal-ligand bond is figured out as 20%.

Similarly, both these paramagnetic impurities VO(II) and Mn(II) are doped in two different struvite analogs to study the ligand symmetry, orientation property and the relaxation time of the host lattice.

Here, the struvite analogs selected are MPPH and CoAPH. Vanadyl ion doped in MPPH gives very interesting and informative results. Three sites are identified in the lattice though the Z value is only two. Two magnetically inequivalent sites turn out to be substitutional and they are found to be orthogonal to each other and the third site appears to be interstitial. This interstitial site is confirmed with the help of the observed super hyperfine spectrum which results from the four protons of the two water molecules. From the calculated spin Hamiltonian parameters, the vanadyl ion is found to have distorted octahedral environment of water molecules which is further confirmed from the optical studies.
Single crystal EPR study of the Mn(II) doped in the CoAPH lattice is quite fascinating as the central metal ion of the lattice Co(II) is also a paramagnetic ion. Surprisingly, Co(II) behaves as a diamagnetic ion at room temperature and its paramagnetic nature is identified by low temperature measurements. EPR study on this lattice confirms the presence of more than one site for Mn(II) ion. But only two of them are followed, as others are difficult to follow, due to their low intensity. It is observed from the EPR studies that the Mn(II) ion has entered the lattice substitutionally and not interstitially. Both the sites are substitutional and they are found to be orthogonal to each other. The presence of two sites is further confirmed from the EPR spectra of the polycrystalline sample. Similar to Mn(II) doped in DAMZ, the D value is found to be positive for the CoAPH lattice also. EPR spectra recorded at variable temperatures confirm the absence of any phase transition down to 77 K. The spin – lattice relaxation times are calculated for the same lattice from the line width measurements.

The thesis provides a rough idea to predict the location of the impurity. Even though it is well known that whenever a paramagnetic impurity is incorporated in a diamagnetic or paramagnetic host lattice, having six ligands, the dopant metal ion prefers a substitutional incorporation at low dopant concentrations. In other cases, it enters either substitutional or interstitial depending on the nature of the ligand. If the ligand is bidentate or multidentate, the dopant prefers an interstitial location, by assuming an identical coordination similar to the host ion. These are the
few observations, which are highlight of the thesis. In addition, low hyperfine coupling constant observed for copper indicates an admixture of ground state with the excited state. Additional work is also promising with PMZD lattice, with the incorporation of paramagnetic ions like Fe(III), Mn(II) etc., and the work is in progress.