INTRODUCTION

1.1. Introduction

Structural and spectra analysis of transition metals with dicarboxylate ligands have continuing attention in the field of chemistry, physics and biology. These complexes, exhibiting extended networks have probable applications in supra molecular frame work, crystal engineering, polymorphs, optical and electrical properties etc [1-2]. The capability of bridging ligand to mediate magnetic coupling between the transition metal centers that it links plays a major role in molecular based magnets. In addition, carboxylic acid, an essential compound for living organisms, has strong coordination ability to various transition metal ions such as Cu(II), Co(II), Ni(II), Zn(II) etc. Some of the transition metals are present naturally, while some others are introduced artificially by synthesis and/or doping in enzymes [3-4]. Transition metal complexes are prevalent interest. These are extensively studied by inorganic chemists, as well as physical, organic, biochemists, pharmacologists, molecular biologist and environmentalists etc. Electron Paramagnetic Resonance (EPR) spectroscopy is an established technique that has been used for recognition of the structure of paramagnetic transition metals. EPR is limited to species with unpaired electrons and it offers information about strength, location, electronic structure of paramagnetic species. EPR is also an extraordinary tool for understanding the structure of metal protein and enzymes [5]. In EPR, pure transition metal complexes offer broad line due to dipole and exchange phenomenon. These systems are known as magnetically concentrated ones. Electron spin relaxation rate enhancement is mainly because of the electron-electron dipole and exchange interactions as they are effective relaxation mechanisms. The broad CW EPR resonance creates difficulties in getting useful information. Spins can be kept apart in systems from interaction by diluting them, known as magnetic dilution. In magnetically diluted systems, there are no electron-electron interactions and hence CW EPR line-width is sharper relative to magnetically concentrated systems and hence, detailed information could be obtained. So, diluting the spins is a simple and successful technique to get valuable information about paramagnetic centers. This thesis illustrates single crystal EPR studies of paramagnetic metal ions in magnetically diluted form.

Malonic acid is a three carbon dicarboxylic acid. It is well known as competitive inhibitor of succinate dehydrogenase. Naturally it is found in biological systems such as legumes and
developing by rat's brain, which indicates that it may play a crucial role in symbiotic nitrogen metabolism [6-8]. Additionally, malonic acid with diethyl ester is used in the synthesis of vitamins B1, B6, barbiturates and numerous other valuable compounds that are important in biological, which have medical applications. For example, malonate is a powerful competitive inhibitor of cellular respiration, because it binds to the active site of succinate dehydrogenase in the citric acid cycle [9]. The malonate ligand occupies one or two coordination positions and neutralizes dipositive charges of the transition metal ion allowing the inclusion of the other ligands in the coordination sphere of the metal. This chelating ligand can act as bridging or blocking one, contributing to the interconnection or isolation of the spin carriers. Thus, combining the malonate with the other bridging and/or blocking ligands, one can prepare monomers, dimers, trimers, tetramers, infinite chains, 2D and 3D arrays [10-14]. Another feature of the malonato bridge is the fact that the magnitude of the exchange interaction depends on the syn-syn, syn-anti, anti-anti bridging modes that it can also be adopted. The nature (ferro- or antiferromagnetic) of the interaction being dependent on the nature of magnetic orbitals of the spin carriers connected by the bridging ligand. These complexes give interest results in the field of chemistry, including synthetic, theoretical, crystallographic and material chemistry that have resulted not only attractive and diversified structures, but also has potential application as medical, photo catalyst material, coordination polymer, absorbent and biologically active ones [15-19]. In addition, the carboxylate group provides an efficient pathway for coupling magnetic centers either ferromagnetic or antiferromagnetically, the coupling constant being influenced by the structural aspects [20-25]. It has been possible to obtain new molecular magnets, even porous magnets, with the flexible malonate dianion. A contrast of cadmium complexes with zinc complexes strongly suggested that the reduced size of the Zn(II) coordination sphere plays an important role in deciding the linkage of metals.

In the present thesis, transition metal ions such as VO(II), Cu(II), Mn(II) and Fe(III) doped in Diaqua(2,2'-bipyridine)malonatozinc(II) (DBMZ) [26], diaquazinc (diaquatibismalonato)zincate (DZDBZ), Diaquacadmium(diaquatibismalonato) cadmate, (DCDBC) [27] and Diaquamalonatozinc(II) (DMZ) [28] have been carried out. These systems are studied mainly by single crystal EPR and also by UV-Visible, FT-IR and powder XRD techniques. The major EPR spectroscopic tool is discussed here and other supportive techniques are presented in the next chapter.
1.2. Electron Paramagnetic Resonance

EPR is an acronym for Electron Paramagnetic Resonance. EPR, also referred as Electron Spin Resonance (ESR) spectroscopy, measures the absorption of microwave radiation corresponding to the splitting of an unpaired electron, when it is placed in a strong magnetic field. EPR is a spectroscopy technique that detects the presence of unpaired electrons in a chemical system. The first observation of an EPR experiment was noticed by a Russian scientist E. K. Zavoisky in 1945 [29]. This can yield important structural and dynamic information, even from ongoing chemical or physical processes without influencing the process itself. This is an ideal tool to complement other analytical methods in a wide range of application areas. These areas include chemistry, physics, materials, biology, medicine and ionization radiation. EPR has developed over past several decades as a technique to provide information on the electronic structure of organic, inorganic, biological, solid state and point defects in various crystals. Additionally, it gives more information about free radicals, biradical triplet excited state, most transition metal ions and rare earth species.

EPR has developed into an effective, versatile, supportive and non-intrusive analytical technique. EPR spectroscopy provides an experimental route to study the magnetic interactions in paramagnetic materials. High sensitivity and the ability to examine low concentration of paramagnetic ions in powders, polymers and frozen solution are key advantage of EPR spectroscopy. Most commonly, these systems should have at least one unpaired electron, i.e., electron spin (S) and S can be any value from 1/2 to 7/2 in increment of 1/2. When the spin is odd, i.e., for example S = 1/2, 3/2, 5/2 or 7/2, spectra are easily obtained at room temperature. However if the spin is even, i.e., for example, S = 1, 2, 3, then the possibility of obtaining spectra depends upon a number of circumstances that are usually not met at room temperature; thus EPR of even spin system is a very specialized one. Additional technique employing both EPR and NMR method (for example ENDOR-electron nuclear double resonance) are available and the present thesis does not carry out such investigations. EPR spectroscopy can be combined with chemical techniques such as trapping to detect and follow free radical reactions in biological systems, etc [30, 31].
1.3. EPR application

EPR spectroscopy has the capacity to give detailed information on the structures of the paramagnetic species and is extremely useful to apply in various fields of science, which includes physics, chemistry, biology, archeology, geology, biomedical, and mineralogy. It is also supported to investigation of radiation-damaged materials and in radiation dosimetry [30-34]. Applications of EPR technique to some important areas are mentioned below:

Chemistry

- Systems with odd number of electrons
- Systems with more than one unpaired interacting electrons (triplet, biradical states)
- Electrochemical oxidation or reduction
- Homogenous catalysis
- Transition ions including actinide ions
- Spin label and spin probe techniques
- Electron spin magnetic susceptibility
- Electron Transfer Reaction kinetics
- Free radicals produced by irradiation techniques
- Catalysis, Organo-Metallic, Molecular magnets etc.,
- Chemical Oscillators

Physics

- Mechnochemical milling process
- Various point defects
- Systems with conducting electrons (semiconductors, metals)
- Optically detected magnetic resonance

Biology

- Photosynthesis
Examining the active site of metalloproteins
Spatially resolved information (EPR Imaging)
Control of irradiated food
Saturation transfer and vector EPR techniques for the study of molecular motions

**Medicine**

Radiation dose assessment
EPR oxygen Mapping (EPROM)
Orientations of ligands around metal proteins
Spin trapping and chemical modification
Free radicals in living tissues

**Ionization Radiation**

Irradiated food
Gamma irradiated L-alanine
Radiation damage
Power saturation

**Material science**

Glasses
Super conductors
Corrosion
Fullerenes
Polymer

In additionally EPR application is also widen to geographical and archeological dating, radiation dosimetry and microscopy magnetic resonance imaging studies and estimating the age of fossils [25].
1.4. **EPR theory** [34-38]

Paramagnetic material with a single unpaired electron has a magnetic moment and spin quantum number $S = 1/2$, with magnetic components $|+1/2>$ and $|-1/2>$. In the presence of an external magnetic field with strength $B_0$, the electron’s magnetic moment aligns itself either parallel ($m_s = -1/2$) or anti parallel ($m_s = 1/2$) to the field, each alignment having a specific energy. The parallel alignments correspond to the lower energy state and the separation between them and the upper state is

$$\Delta E = g_e \mu_B B_0$$

(1.1)

where $g_e$ is the electrons $g$ factor (also known as Lande $g$-factor) and $\mu_B$ is the Bohr magneton. The equation implies that the splitting of the energy level is directly proportional to the magnetic field strength. An unpaired electron can move between the two energy levels by either absorbing or emitting electromagnetic radiation of energy $E = h\nu$. This will lead to the resonance condition $h\nu = g_e \mu_B B_0$. Experimentally, this equation permits a combination of frequency and magnetic field values, but majority of EPR measurement are made with microwaves in the 9000 - 10000 MHz (9-10 GHz) region, with field corresponding to about 3500 G (0.35T).

EPR spectra can be generated by either varying the frequency incident on a sample while holding the magnetic field constant, or doing the reverse. In practice, it is usually the frequency that is kept fixed. By varying the external magnetic field, the gap between the $|+1/2>$ and $|-1/2>$ energy states is widened until it matches the energy of the microwaves. At this point, the unpaired electron moves between the two spin states. Since there are more electrons in the lower state, due to Boltzmann distribution, there is a net absorption of energy that is being monitored. Most EPR spectra are recorded only as a first derivate to get accurate magnetic field positions. In few cases, second derivate spectra are also recorded.

A complete analysis of the EPR spectrum leads to a very accurate determination of bonding parameters and the electronic structure of the ground state, which is the unique characteristic of EPR techniques. EPR is sensitive to the charge in symmetry of the environment. A general consideration of the interaction involved in the case of a paramagnetic species in a crystal field is formulated in terms of a generalized Hamiltonian. The spin Hamiltonian consist of various terms, which have been arisen due to different types of interactions between electron spin or another electron spin and nuclear spin, and nuclear spin either with applied magnetic field or another nuclear spin.
1.5. Selection Rules

In EPR, allowed transition corresponds to the change of only $m_s$ i.e., $\Delta m_s = \pm 1$ and $\Delta m_I = 0$. This means that only the electronic spin "flips", whereas the nuclear spin remains unchanged.

1.6. Spin Hamiltonian

In general, most EPR data can be described in terms of “Spin-Hamiltonian” involving smaller number of terms by using an effective fictitious spin, which does not require a full knowledge of spin orbit coupling, the strength of crystal field splitting, etc. This Hamiltonian gives electron Zeeman interaction energy only and so, it is otherwise called Zeeman interaction Hamiltonian. Basically, it represents all possible interactions that affect the spin system and give rise to its energy states. For the most general hypothetical case with electronic spin $S > 1/2$, and nuclear spin $I \geq 1$, the effective spin Hamiltonian consists of the following terms:

$$\mathcal{H}_S = \mathcal{H}_{ze} + \mathcal{H}_{ss} + \mathcal{H}_{hfs} + \mathcal{H}_{nz} + \mathcal{H}_Q$$

$\mathcal{H}_{ze}$ = Electron Zeeman interaction

$\mathcal{H}_{ss}$ = Electron Spin-Spin interaction

$\mathcal{H}_{hfs}$ = Electron Spin-Nuclear Spin Hyperfine interaction ($I \neq 0$)

$\mathcal{H}_{nz}$ = Nuclear Zeeman interaction

$\mathcal{H}_Q$ = Nuclear Quadrapole interaction

1.6.1. Zeeman interaction $\mathcal{H}_{Zee}$

This happens due to the interaction of the external magnetic field with the spin and orbital magnetic moment of the electron and nuclear spin magnetic moment and is given by

$$\mathcal{H}_{Zee} = \beta (L + 2S) B - g_n \beta_n B \sum I_i$$

where $\beta_n$ is the nuclear magneton, $g_n$ is the nuclear g-value and $I_i$ are the various magnetic nuclear spins. The first term is known as the electron Zeeman interaction. The second term, known as nuclear Zeeman interaction, is of minor important in EPR, expect in cases where the hyperfine coupling is much smaller than the nuclear Zeeman interaction.
1.6.2. Spin orbit interaction $\mathcal{H}_{LS}$

This represents the coupling between the magnetic moments arising from the spin and orbital motion of the unpaired electron and is written as

$$\mathcal{H}_{LS} = \sum_{i,j,k} a_{j,k} l_j S_k$$

(1.3)

The above terms can be given in terms of the one electron spin orbit coupling constant $\xi_i$ as,

$$\mathcal{H}_{LS} = \sum \xi_i l_i S_i$$

(1.4)

And for the Russell–Saunders scheme, the expression further changes to,

$$\mathcal{H}_{LS} = \lambda \ L.S$$

(1.5)

where, $\lambda$ is the spin orbit coupling constant of the ion. The spin orbital coupling constant is a function of the effective nuclear charge. For more than half filled shells, $\lambda$ is negative and for less than half-filled shells, $\lambda$ is positive.

1.6.3. Spin-spin interaction $\mathcal{H}_{ss}$

When more than one unpaired electrons are involved in the systems, with ground state triplet or higher spin multiplicity, direct dipole - dipole interaction among these spins leads to the splitting of the spin-state via spin - spin interaction given by

$$\mathcal{H}_{ss} = (g\beta)^2 \sum_{j>k} \sum_{j,k}$$

(1.6)

When the external magnetic field is much stronger than the magnitude of spin-spin coupling constant, the above vector products can be expanded to give

$$\mathcal{H}_{ss} = \cdots$$

(1.7)

where, $\theta$ is the angle between the external field and vector joining $S_j$ and $S_k$.

1.6.4. Hyperfine interaction $\mathcal{H}_{hfs}$

This is a zero field type interaction connecting the electron magnetic moments and the associated nuclear magnetic moments. This consists of an isotropic Fermi contact term for s-
type spin densities and a pure dipole - dipole type interaction described by a tensor due to unpaired p, d and f type spin densities. These interactions are written as;

\[ \mathcal{H}_{S,I} = g \mathbf{B} \cdot \mathbf{\alpha} \cdot \beta \left[ \frac{1}{2} \sum \delta(r_{ij}) \mathbf{I}_i \cdot \mathbf{S}_j \right] \] (1.8)

The first term describes an interaction of two point dipoles and the second containing the Dirac delta function, which when integrated with the wave function vanishes except at \( r_{ij} = 0 \), corresponds to the isotropic interaction. Thus, in the non-relativistic approximation only, s-orbital can contribute to isotropic coupling to the concerned nuclei.

1.6.5. Nuclear Quadrupole Interaction \( \mathcal{H}_Q \)

This interaction is relevant only to systems having nuclei with spin \( I \geq 1 \) and arises as a result of the interaction of the nuclear electric quadrupole moment with the electric field gradient at the nucleus due to the surrounding electrons. It is expressed as

\[ \mathcal{H}_Q = \sum_{ij} \left[ e^2 Q_i / 2I_i (2I_i - 1) \right] \left[ r_{ij}^2 I_i (I_i + 1) - 3(r_{ij} I_i) I_i \right] \] (1.9)

where \( Q \) is the nuclear electric quadrupole moment.

In Dyad operator notation, the above equations can be expressed as

\[ \mathcal{H}_S = \beta \mathbf{e} B \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{Q} \cdot \mathbf{I} + \ldots \] (1.10)

where \( g \), \( A \), \( D \) and \( Q \) are second rank tensors, whose principal axes need not coincide. These correspond to the electronic \( g \)-tensor, hyperfine tensor, zero field tensor and quadrupole coupling constant tensor respectively.

The idea of the fictitious spin can be discussed in a detailed fashion. In the case of a quantum state described by \( J \) splits it into \( (2J+1) \) level in an external field, similarly a system designated with the fictitious spin \( S \) splits into \( (2S+1) \) levels and transitions are allowed between these according to the selection rules. The only difference between the true spin \( S \) and fictitious \( S' \) is that the latter defines the effective spin angular momentum obtained due to admixture of higher lying states into the ground state via spin-orbit coupling, and hence effectively takes into account of the effect of crystal field terms, and spin orbital term of the generalized Hamiltonian. Since the isotropic \( g \)-factor of a free electron is modified into a tensor when orbital momentum is not completely quenched in the principal axis system of the \( g \)-tensor, the Hamiltonian is written as
\[ \mathcal{H} = \beta (B_x g_{xx} S_x + B_y g_{yy} S_y + B_z g_{zz} S_z) \]  

(1.11)

If the tensor is cylindrically symmetric, \( g_{xx} = g_{yy} = g_{zz} = g \) and \( B_x = B_y = B_z \), then

\[ \mathcal{H} = \beta [BgS] \]  

(1.12)

And if the tensor is axially symmetric,

\[ \mathcal{H} = \beta \left[ B_z g S_z + g \mu (B_x S_x + B_y S_y) \right] \]  

(1.13)

Likewise, the hyperfine terms which consist of a dipolar part and isotropic part is written generally as,

\[ \mathcal{H} = A_{xx} I_x S_x + A_{yy} I_y S_y + A_{zz} I_z S_z \]  

(1.14)

If the unpaired electron is purely s-type, then

\[ \mathcal{H} = a I_z S_z \text{ and } a = (8\pi/3)g\beta g\beta n |\psi(0)|^2 \]  

(1.15)

where \( |\psi(0)|^2 \) is the squared amplitude of the unpaired s-electron density at the nucleus. Isotropic hyperfine interaction is due to (a) direct unpaired spin density in an s-orbital or in a molecular orbital (M.O) with s-orbital contribution (b) spin polarization, due to isotropic hyperfine coupling in an isolated paramagnetic atom or ion, where the electron is in a p- or d- orbital arises via polarization of core s-electron and (c) also configuration interaction between a ground state M.O. orbital with no s-orbital contribution and state with finite s-orbital contribution.

Dipolar coupling arises due to point dipole interaction between p or d orbitals with the nucleus and follows a \((3\cos^2\theta-1)\) variation given by

\[ \mathcal{H}_d = g\beta g\beta n (3\cos^2 \theta - 1) \langle 1/\langle r^3 \rangle \rangle \]  

(1.16)

In \( p^3 \) or \( d^5 \) high spin configuration, due to spherical charge distribution, dipole coupling vanishes. Also paramagnetic systems in solution, when the system tumbles rapidly, it average to zero, being represent by a trace-less tensor.

The sign of the experimental principal values of the hyperfine tensor cannot be determined from the EPR spectra very easily. However, if the isotropic coupling can be independently determined, one can always calculate the ratio of unpaired p and s densities in simple free radicals. Often hyperfine coupling to ligand-magnetic nuclei in transition metal complexes, when the unpaired electron formally occupies a metal orbital and orbital can be lead to an estimate of the covalence of the metal ligand bonds.
In system with more than one unpaired electron, the spin degeneracy is removed even in the absence of external magnetic field by second spin-orbital coupling known as the zero field interaction. This is also a dipolar type interaction and is expressed in the spin Hamiltonian as

$$\mathcal{H}_{ss} = D[S_x^2-\frac{1}{3}S(S+1)]+E(S_x^2-S_y^2)$$

$$= D_{xx}S_{xx}^2+D_{yy}S_{yy}^2+D_{zz}S_{zz}^2$$

(1.17)

The $D_{ii}$'s are the principal values of the D-tensor and E is an asymmetric parameter depending on the deviation of the D-tensor from cubic symmetry. The relative magnitudes of D and $g\beta B$ are to be considered in any perturbation treatment of the spin Hamiltonian.

The quadrupolar term in the spin Hamiltonian is quite analogous to the zero field terms and is given by

$$\mathcal{H}_Q = Q_{xx}I_x^2+Q_{yy}I_y^2+Q_{zz}I_z^2$$

$$= Q'[I_z^2-\frac{1}{3}I(I+1)]+Q''[I_x^2-I_y^2]$$

(1.18)

Where, $Q_{ii}$'s are the principal values of the quadrupole coupling constant tensor. Here, $Q'$ is similar to D and $Q''$ to E. In single crystals, especially when the external field is perpendicular to the symmetry axis, the analysis becomes very difficult due to the presence, sometimes, of intense forbidden transition [36].

The spin Hamiltonian parameters can be derived theoretically by knowing the ground state molecular orbital and optical spectroscopic data, coupled with perturbation theory [39, 41]. It is also possible to obtain bonding parameters for transition metal complexes from EPR data.

1.7. Crystal field parameters for d electron

In general, many complexes possess symmetry lower than octahedral. Deviations from octahedral symmetry are usually treated as perturbations on the symmetry, which causes splitting in the degenerate levels. In the present investigation in all lattices, the symmetry of the metal ions is lower than the octahedral symmetry. In such a situation, the ground state is not purely due to a single d-orbital, because the orbital contribution to the spin Hamiltonian is due to the mixing of the exited state wave function with the ground state through spin orbital coupling. Therefore, in the most general situation, the ground state is the linear combination of the five d orbitals. Without limiting to any symmetry considerations, the coefficients of the d-orbitals and hence the ground state can be calculated using Swalen’s procedure [42]. In this method, the
experimentally observed g-values are used to determine the five coefficients of the Kramers’ doublet. There are only three g-values and normalization condition to determine five coefficients.

1.8. Jahn Teller and Kramers’ Theorem

Two important theorems are necessary while discussing the EPR theory. First one is Jahn-Teller, which states that “For a non-linear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy and lower the energy”. In other words, if a molecule or crystalline defect has orbital electronic degeneracy when nuclei are in a symmetric configuration, then the molecule or the defect is unstable with respect to at least one asymmetric displacement of the nuclei which lifts the degeneracy. The theorem has been exception linear molecule [43].

Kramers’ theorem states that a purely electrostatic field can never reduce the degeneracy of the system, if it has an odd number of electrons [44]. Such degeneracy as remains (generally two fold) can be lifted only by an external magnetic field. He showed that a system containing an odd number electrons, even with no symmetry, and with no magnetic field, must be at least doubly degenerate. A non Kramers’ centre will have $S = 1, 2, 3$, etc. A corollary of this is that systems with odd numbers of electron will relax differently from one with even numbers of electrons.

1.9. Magnetically and chemically inequivalent sites

A paramagnetic system with anisotropic g and A tensor give rise to EPR resonance depending on the orientation of the magnetic field B with respect to the tensor axes. Depending on the space group and the number of molecule per unit cell (Z), several different spatial orientation of the paramagnetic sites in the single crystal are possible. Species that are chemically identical (i.e., they are described by the identical spin Hamiltonian parameters) but are spatially oriented differently are referred to as magnetically distinct sites. It is also possible that due to charge compensation process [45, 46] in the lattice, depending upon different relative configurations of the vacancy directions, there exist many different sets of spin Hamiltonian parameters. The species themselves would be expected be identical when the charge
compensating vacancies are not considered. Such sites are termed as chemically distinct sites. The chemically distinct sites are necessarily magnetically distinct, whereas the converse need not necessarily hold.


References


