

Article Arrival Date

15.08.2020

Article Type

Research Article

Article Published Date

15.09.2020

Doi Number: <http://dx.doi.org/10.38063/ejons.328>

MOLECULAR STRUCTURAL ELUCIDATION AND LOCATION OF MN(II) ION IN DIAQUAZINC(DIAQUABISMALONATO)ZINCATE BY SPECTROSCOPIC STUDIES

K. Parthipan^{a}*^aDept of Chemistry, SIVET College, Gowrivakkam, Chennai-600073, India

Email id : psr12in@gmail.com

ORCID: 0000-0003-1505-5410

ABSTRACT

Single crystal EPR, optical, FT-IR and powder XRD studies of Mn(II) ion incorporated diaquazinc(diaquabismalonato)zincate were carried out at room temperature to get understanding about the dopant. Observed EPR spectrum result shows 30 lines hyperfine patterns, it indicates manganese present in the host lattice with large D value. The spin Hamiltonian parameter have been evaluated using three orthogonal crystal rotations: $g_{xx} = 1.997$, $g_{yy} = 2.004$, $g_{zz} = 2.008$; $A_{xx} = 8.32$, $A_{yy} = 8.54$, $A_{zz} = 9.74$; $D_{xx} = 35.4$ $D_{yy} = 7.46$ $D_{zz} = -42.85$ mT. The large zero field tensor due to steric interaction of malonato bridge. The direction cosines of spin Hamiltonian parameters (g, A and D) were propose that Mn(II) ion has entered the lattice substutionally and precise direction has been establish with help of position of atoms in host lattice. The covalency of Mn(II)ligand bonds were estimated using Matumura's plot. The observed optical band were assigned as transition from the ${}^6A_{1g}(S)$ ground state to various excited quartet levels of Mn(II) in distorted octahedral symmetry. The theoretical band positions were examined by energy expression and its good agreement with experimental values. The crystal field (Dq) and Racah inter electronic repulsion parameters were studied as well.

Keywords: EPR Spectroscopy, Manganese, Spin Hamiltonian, Zinc malonate

1. INTRODUCTION

Structural investigations of Cu(II) and VO(II) ion in zinc and cadmium malonato complexes were reported [1-2]. The results designated that the dopant has entered the lattice substutionally, which was a rare surveillance due to the structural constricts. In continuation of our effort to malonato complexes due to considerable important in the field of crystal engineering, supramolecular architecture, molecular electronics, catalysis, magnetic materials. In addition carboxylic acid were

essential compounds for living organism and also strong coordination ability to various transition metal ions such as Cu(II), Co(II), Ni(II) etc, malonic acid was also a good chelating ligand leading to form homometallic chain compounds. Due to the fact that malonate are suitable aspirant for the examination of exchange coupling interaction between the adjacent metal, have played prominent role for many biological system [3-5]. For examples, zinc malonate used as dental relevances, platinum malonate complexes have employed as treatment of malignant tumor. Malonic acid is well known competitive inhibitor of symbiotic nitrogen metabolism occurs in large amount in the living systems naturally, especially in rat's brain. The malonate ligand is a dicarboxylic acid group with single behavior different from the other dicarboxylic ligands. It can exhibits different coordination modes such as (i) bidentate [η^5 -chelation], (ii) bidentate [η^5 -chelation] + unidentate and bidentate [η^5 -chelation] + bis(unidentate). From coordination point of views, malonic acid have two neighboring carboxylic acid groups is very flexible to form complexes with transition metals. This chelating ligand can act as bridging as well blocking ligand to generate metal organic frame works of different dimensionalities may lead to interesting architecture. Thus, combining the malonate with the other bridging or blocking ligands are also able to prepare monomers, dimers, trimers, tetramers, infinite chains, 2D and 3D arrays. Another feature of the malonate bridge is the magnitude of exchange interaction which depends on the syn-syn, syn-anti, anti-anti bridging modes also it adopts. The nature (ferro- or antiferromagnetic) of the interaction being dependent on the nature of the magnetic orbitals of the spin carriers connected by the bridging ligand. In addition, the carboxylate group provides an efficient pathway for coupling magnetic centers either ferromagnetic or antiferromagnetic [6-7]. Different topologies have been examined for the homobimetallic cobalt, nickel and manganese complexes. Most of these complexes have been magnetically characterized and they exhibit ferromagnetic coupling through carboxylate bridged [8-9]. Based on above fascinating phenomenon, we have prepared diaquazinc(diaquabismalonato)zincate and structurally characterized by single crystal XRD. Diaquazinc(diaquabismalonato)zincate (after abbreviated as DZDBZ) is chosen as good diamagnetic host lattice and introduced another paramagnetic ion in this lattice. Among the transition metal ions, we preferred manganese(II) ion was preferred, because the shell contains five unpaired electron ($S = 5/2$) with half filled configuration and resultant angular moment is zero. The ground state of Mn(II) is $^6S_{5/2}$. EPR study of Mn(II) have been done quite expansively in the exploration of structural and dynamic aspect of crystalline state since zero field splitting in these ions were sensitive to even small distortions. The study were further widen to ascertain the location of Mn(II) present in DZDBZ and find out the spin Hamiltonian parameters, predict distortion and bonding parameters also discussed.

2. EXPERIMENTAL

Zinc acetate and malonic acid were purchased and used without purification. The amount of zinc in DBDBZ was determined by Gravimetric using 8-hydroxy quinoline as well complexometric titration using EDTA. The CHN microanalyses were carried out on an elemental analyzer and the content of Mn(II) were determined by atomic absorption spectrophotometer. Optical absorption spectrum was recorded at 300K using a Varian Cary 5000 UV Visible near infrared spectrophotometer in the range of 200-1000 nm. The FT-IR spectra were recorded for doped and undoped materials on a Shimadzu FT-IR 8300/8700 spectrometer with 4 cm⁻¹ resolution, automatic gain, and 20 scans in the frequency range of 4000-400 cm⁻¹. The measurements are made using almost transparent KBr containing fine powdered sample. Powder XRD measurements were carried out for doped and undoped materials on a PANalytical X'pert PRO diffractometer with Cu K α radiation of wavelength 0.15406 nm and 2 θ range between 5 and 10 75°. EPR spectra were recorded on a JEOL JES –TE100 ESR spectrometer 11 operating at the X-band microwave frequency, equipped with 100 kHz 12 field modulation for obtaining first derivative EPR spectrum. DPPH (2,2- diphenyl-1-picrylhydrazyl) with a g-value of 2.0036 is used for g-factor calculations. Angular variations are made by rotating the crystal along the three mutually orthogonal axes a, b, c* in 10° interval. Isofrequency plots of each plane were simulated using program EPR-NMR [15]. The EPR spectrum of powder sample was simulated using SimFonia program developed and supported by Bruker Biospin.

732

3. CRYSTAL STRUCTURE

DZDBZ [Zn(H₂O)₂(Zn(mal)₂(H₂O)₂)]_n belongs to monoclinic with space group P2₁/n having unit cell parameters a = 0.7305 (4), b = 0.7412 (4), c = 1.1075 (7) nm; β = 95.364(5)° and Z = 2. The central zinc atom lies in an inversion center (Fig.1a-1b). The oxygen atoms can be divided into four sets according to their bonding features, namely, terminal, bi-bridging, tri-bridging and penta-bridging oxygen atoms. All Zn–O bond distances are within the expected ranges. The dihedral angle between the rings C1-C2-C3-O1-O2-Zn and C1d-C2d-C3d-O1d-O2d-Zn is 0.02(1)°, shows that both rings are co-planar. The Zn1 center is octahedral, with O(1) and O(2) of two bidentate malonate anions at basal sites (distances of 2.046(3) and 2.048(3) Å, respectively). The O(4) atom of the malonate ligand is linked to the zinc atom Zn2 forming a network. The Zn1 and Zn2 atoms are coordinated to two O(4) and two O(5) of different malonate anions and two O(6) of the lattice water molecule, the average distance being 2.123 Å. Coordination is completed via O(4) atoms at distances of 2.137(3) Å from other malonate anion. These bridging arrangements by carboxylate groups form infinite sheets in which the closest Zn...Zn separation is 5.20 Å. All the bond angles around Zn are close to 90°. The

bond angle and bond length of DZDBZ is given in Table (1a-1b) respectively. In all the hydrogen bonds, the water oxygens act as donor atoms, and the carboxylate act as acceptor atoms. The largest donor acceptor distance is 2.15(4) Å between O3 and O4. In this structure, the malonate groups have an extended conformation. The average C-O distances are 1.26 Å, and the average O-C-O angles are 122°. These values agree well with that of other previously reported malonate-containing metal complexes [10]. Two water molecules and four coordinated malonate-oxygens form a distorted octahedral surrounding around the zinc atom. The values of the Zn-O (malonate) bond distances are [2.137(3) and 2.147(3) Å,] this distances are somewhat similar to the values of the Zn-O(water) ones [2.086 Å]. The best equatorial plane around the zinc atom is defined by the O(4), O(5), O(4c), and O(5c) set of atoms, in this plane all the atoms are in planes, there is no slight deviation from the metal atom as well as from the other atoms. Each malonate group adopts bidentate and monodentate coordination modes towards zinc atoms. This ligand adopts envelope conformation, with the puckering parameters q_2 and φ and the smallest displacement asymmetric parameters, Δ_s , as follows: $q_2=0.443(3)$ Å, $\varphi=359.6(5)^\circ$, $\Delta_s(C2)=0.5(4)$, in which only the methylene group is significantly displaced from the chelating six-membered chelate. The atom O3 acts as a donor to the atom O4 of the neighbor molecule. This hydrogen bond is involved in a motif C(6) forming an infinite chain along a axis and also the intra molecular O6-H6A...O2 hydrogen bond forms a S(6) ring motif. In addition to the vander wals interactions, the crystal packing is stabilized by O-H...O hydrogen bonds forming a three dimensional network.

733

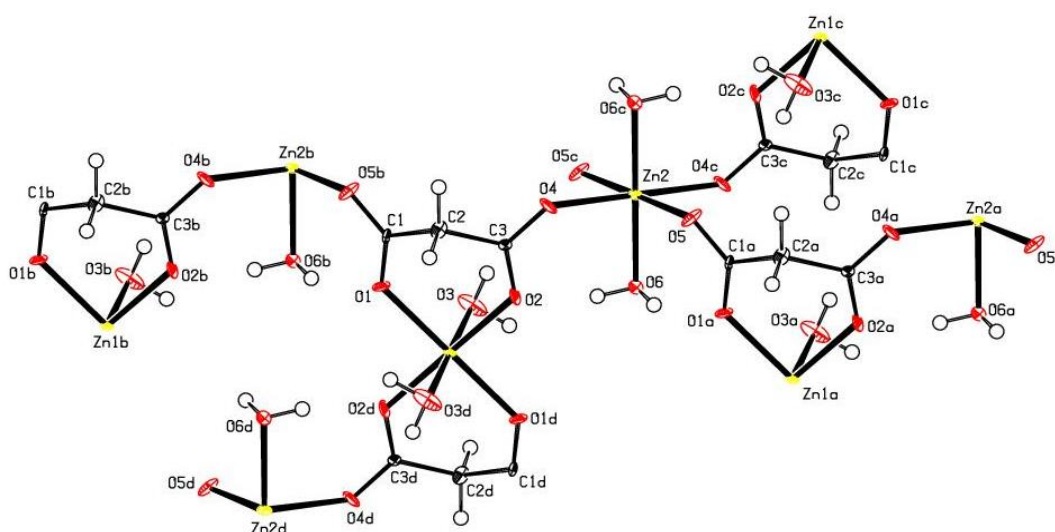


Fig. 1a The molecular structure of $[[Zn(H_2O)_2(Zn(mal)_2(H_2O)_2)]_n$

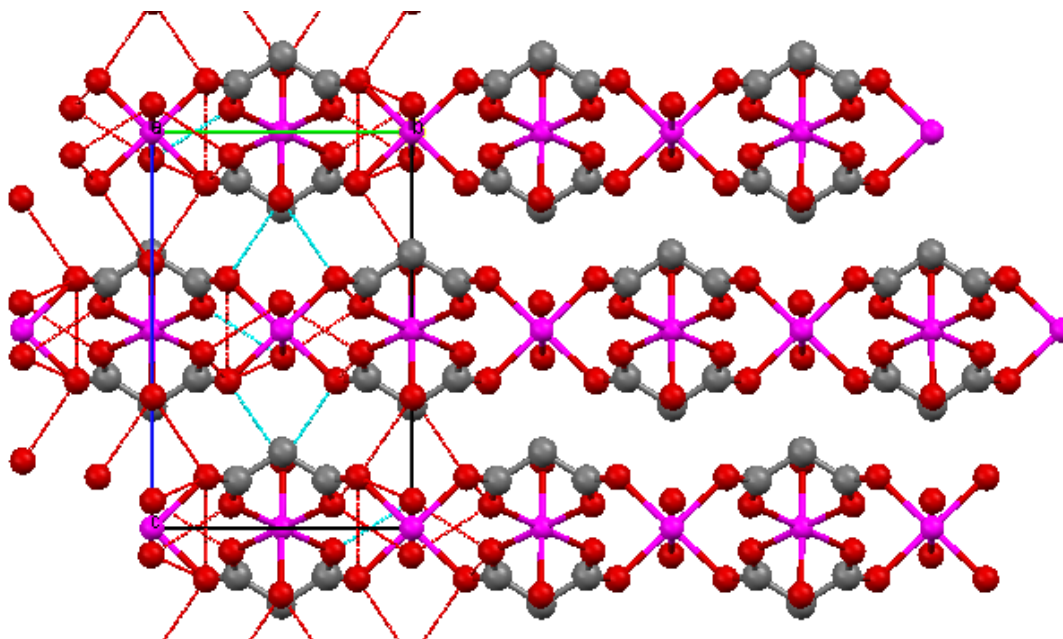


Fig. 1b: The molecular packing diagram for DZDBZ along b-axis in a crystal.

1	Zn(1)-O(2)	2.047(3)
2	Zn(1)-O(1)	2.047(3)
3	Zn(1)-O(3)	2.153(3)
4	Zn(2)-O(6)	2.086(2)
5	Zn(2)-O(4)	2.138(3)
6	Zn(2)-O(5)	2.146(3)

734

Table 1a: Bond length for DZDBZ $[[\text{Zn}(\text{H}_2\text{O})_2(\text{Zn}(\text{mal})_2(\text{H}_2\text{O})_2)]_n$

1	O(2)-Zn(1)-O(1)	90.03(9)
2	O(2)-Zn(1)-O(3)	92.27(12)
3	O(1)-Zn(1)-O(3)	91.84(12)
4	O(6)-Zn(2)-O(4)	94.00(11)
5	O(6)-Zn(2)-O(5)	92.92(11)
6	O(4)-Zn(2)-O(5)	92.71(9)
7	C(3)-O(2)-Zn(1)	127.6(3)
8	C(1)-O(1)-Zn(1)	127.0(2)
9	C(3)-O(4)-Zn(2)	126.2(3)
10	C(1)-O(5)-Zn(2)	126.7(3)

Table 1b: Bond angles for DZDBZ $[[\text{Zn}(\text{H}_2\text{O})_2(\text{Zn}(\text{mal})_2(\text{H}_2\text{O})_2)]_n$

4. RESULTS AND DISCUSSION

4a. Optical absorption studies

Optical spectrum of Mn(II)/DZDBZ, recorded at room temperature is depicted in Fig 2. The spectrum exhibits five bands at 693, 558, 410, 342, 243nm. Fig 2 shows characteristic features of Mn(II) in octahedral symmetry. The absorption bands at 14 430, 17 921, 24 390, 29 239, 41 152 cm^{-1} are in the order of d-d transition of Mn(II) ion. From the nature and position of the band observed, these bands are attributed to Mn(II) in distorted octahedral symmetry. The first band is CT band and remaining four bands have been assigned to ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{1g}(\text{G})$, ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{E}_g(\text{G})$, ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{E}_g(\text{D})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}(\text{G})$ transitions respectively, with the help of Tanabe Sugano diagram. The energy matrices for the d^5 configuration inclusive of Trees correction were given by mehra [11]. In the analysis of optical absorption spectrum, trees correction parameter has been included in addition to the crystal field parameter Dq and racah interaction parameters B and C. The values which give best fit with observed data are $Dq = 800$, $B = 837$ and $C = 2905 \text{ cm}^{-1}$. The band data are well matched with reported in literature. The value of the interelectronic repulsion parameter B (837 cm^{-1}) obtained in the present work, when compared with the free ion value (960 cm^{-1}), is decreased by an amount of 13%. This decreasing is caused by influence of bond covalency.

735

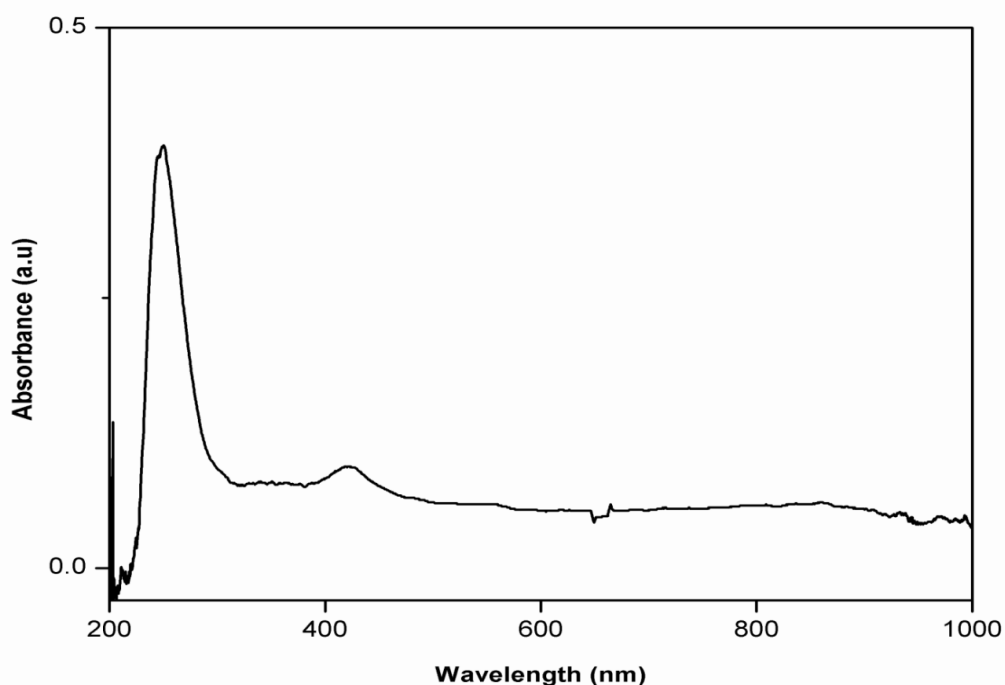


Fig. 2: Powder optical absorption spectrum of Mn(II) doped DZDBZ at room temperature.

4b. FT-IR and powder XRD

The FT-IR spectrum of DZDBZ and Mn(II) doped DZDBZ are recorded at room temperature and illustrated in Fig. 3. The FT-IR spectrum of DZDBZ shows characteristic bands for -OH, OH₂, COO⁻, -CH₂- and Zn-O [12]. FT-IR spectrum of Mn(II) doped DZDBZ also shows comparable characteristic bands with DZDBZ and slight wave number shift observed due to low concentration of Mn(II) impurity. The observed FT-IR bands and their tentative assignments for DZDBZ and Mn doped DZDBZ are depicted in Table 2a. The powder XRD pattern of Mn(II) doped DZDBZ is recorded at room temperature and depict in Fig. 4. Lattice parameter also calculated along with single crystal data of DZDBZ are listed in Table. 2b. According to the powder XRD measurements, the Mn(II)/DZDBZ has the identical lattice parameters as the pure DZDBZ, this clearly says that paramagnetic impurity does not rework the structure of DZDBZ due to low concentration of Mn(II) impurity.

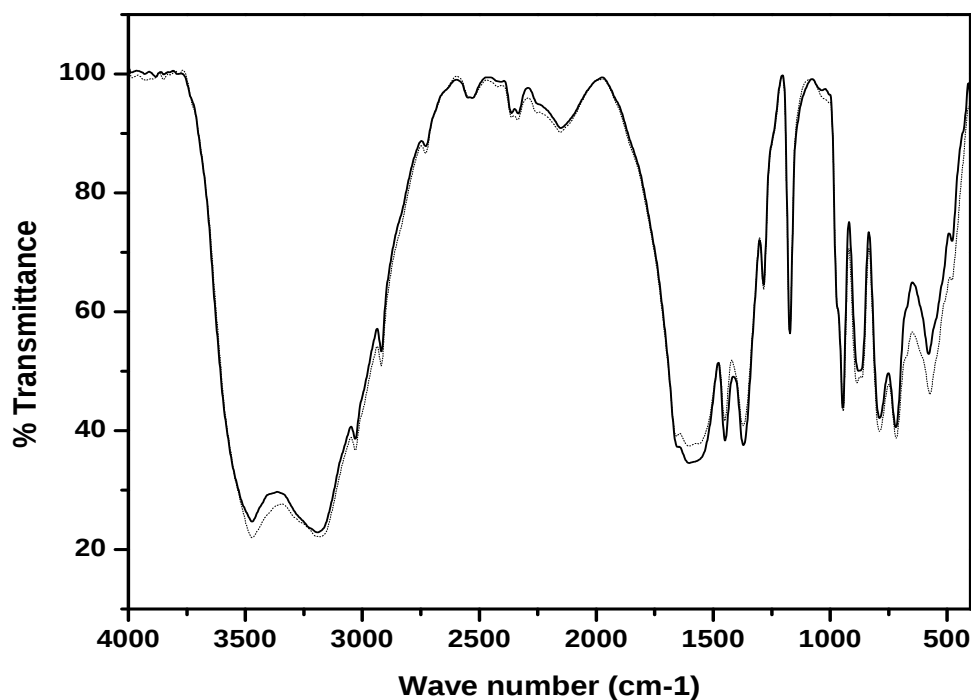


Fig. 3: FT-IR spectra of pure (top) and Mn(II) doped DZDBZ (bottom) at room

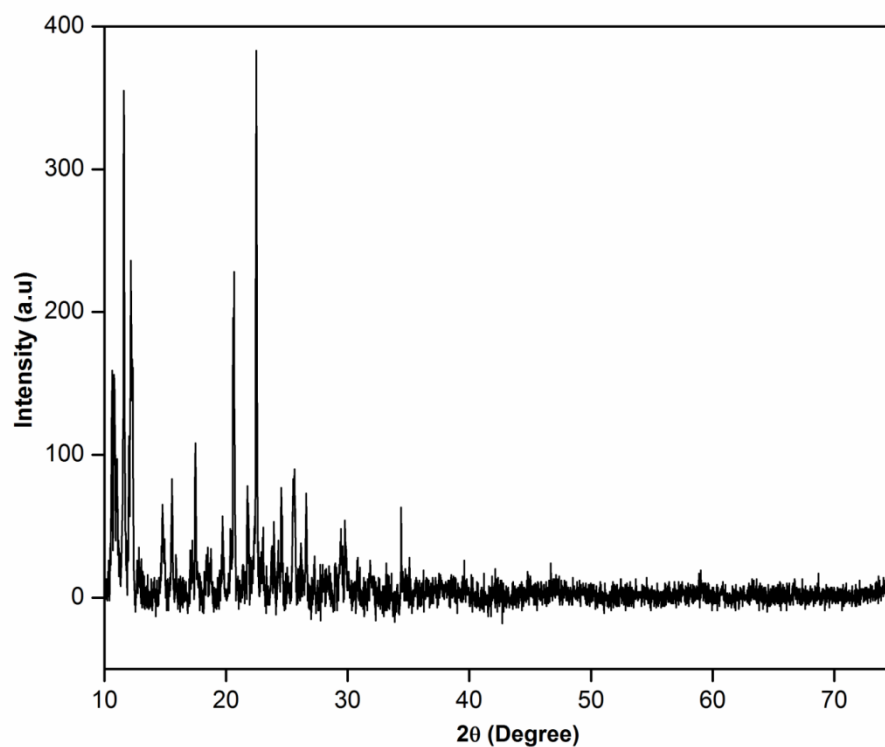


Fig. 4: Powder XRD pattern of Mn(II) doped DZDBZ.

Assignments	DZDBZ (cm^{-1})	Mn(II) /DZDBZ (cm^{-1})
Zn-O	722, 572	719, 563
Zn – O + O – C– O	793	791
(C = O) + (C – H)	1588	1591
OH ₂	3246, 3105	3838, 3118
-CH ₂	1184, 2851	1192, 2859
-OH	3471, 3874	3469, 3661

Table 2a: Observed FT-IR bands and their tentative assignments for DZDBZ and Mn(II) doped DZDBZ.

Lattice parameter (nm) of DBDBZ from single crystal XRD	Lattice parameters (nm) calculated from powder XRD	
DZDBZ	DZDBZ	Mn(II) doped DZDBZ
a = 0.7305	a = 0.7406	a = 0.7423
b = 0.7412	b = 0.7458	b = 0.7494
c = 1.1075	c = 1.0856	c = 1.0782

Table 2b: The calculated lattice parameters of DZDBZ and Mn(II)-doped DZDBZ from powder XRD, along with single crystal XRD of DZDBZ.

4c. EPR studies

Manganese ion having $3d^5$ electronic configuration with $^6S_{5/2}$ ground state (based on Hund's rule). In crystalline field low symmetry, the ground state splits into three Kramers doublet specifically $\pm 1/2$, $\pm 3/2$ and $\pm 5/2$. In the applied magnetic field, the degeneracy completely eliminated and it gives five fine structure transitions. Fig. 5 illustrates the schematic energy level diagram for Mn(II) ion showing electronic levels in zero and strong magnetic fields together with splitting due to nuclear spin. Each line will be further split into six hyperfine lines then totally it gives 30 lines [13-15]. A good shape with appropriate size Mn(II) doped DZDBZ single crystal is selected and fixed to EPR cavity. The EPR spectra are recorded by rotating the crystal in the magnetic field about three mutually perpendicular axes namely a, b, c^* axes for every 10° interval. Here a and b is crystallographic axes a and b, c^* is perpendicular to axis b and a. Single crystal EPR spectrum of Mn(II) doped DZDBZ at room temperature shows five set of six lines each. Due to interaction of electron spin ($S = 5/2$) and nuclear spin ^{55}Mn ($I = 5/2$) resulting 30-line pattern. When the crystal Mn(II) doped DZDBZ c^* axis parallel to applied magnetic field (B), the observed EPR spectrum is shown in Fig. 6a. Two more spectra are resulted when the crystal is rotated in planes bc^* and ab are shown in Fig. 6b and Fig. 6c. The widespread high spin Mn^{+2} have $S = 5/2$ and $I = 5/2$, in the absence of applied magnetic field the ground state $^6S_{5/2}$ splits into three Kramers doublet levels resultant to $|\pm 1/2\rangle$, $|\pm 3/2\rangle$, $|\pm 5/2\rangle$, with spacing $2D$ and $4D$ respectively, where D is zero field splitting parameter. When an external magnetic field is applied, these doublets split and transition between them, i.e., $|-5/2\rangle \rightarrow |-3/2\rangle$, $|-3/2\rangle \rightarrow |-1/2\rangle$, $|-1/2\rangle \rightarrow |1/2\rangle$, $|1/2\rangle \rightarrow |3/2\rangle$ and $|3/2\rangle \rightarrow |5/2\rangle$ give rise to five fine structure lines resulting in 30-lines pattern. In some of orientations more than 30 lines are noticed indicating the

presence of more than one site. However, the second site could not be followed due to its weaker intensity and overlying with first site during crystal rotations. It is almost impossible to follow during all the rotations. A plots of angular variation EPR spectrum of Mn^{+2} doped DZDBZ single crystal in the ac^* and ab planes are shown in Fig. 6a and 6b. In those figures, the solid line represents theoretical and solid point represents experimental values. A systematic study of angular variation plots of EPR spectra will give information regarding the principal axes of the complex that Mn(II) in the form in the crystal. Fig. 6a clearly elucidates that low field and high field transition are completely resolved in ac^* plane. The isofrequency plot of Mn(II) doped DZDBZ in ab plane shows (Fig 7a-7c) the fine structure lines do not cross because D_{xx} and D_{yy} have same sign. The angular variation of fine structure and hyperfine lines in the two orthogonal planes are fitted with the help of program EPR-NMR to the spin Hamiltonian [15] (including second order effects).

$$H = \beta(g_x B_x S_x + g_y B_y S_y + g_z B_z S_z) + (A_x S_x I_x + A_y S_y I_y + A_z S_z I_z) + D[S_z^2 - 1/3S(S+1)] + E[S_x^2 - S_y^2]$$

Here first term represent the Zeeman energy, and the second term is due to hyperfine interaction. The axial and rhombic components of the zero field splitting are represented by the third and fourth terms. S_x , S_y , S_z are the spin operators with respect to the cubic field axes. The parameters D and E are zero field splitting due to rhombic and axial crystalline field matrix and E represents the deviation from the axial symmetry. Using the above equation to calculate spin Hamiltonian parameters are shown in Table 4 along with respective direction of cosines. From Table 4 clearly says that $g/A/D$ is nearly coincident, and additional geometry of Mn(II)/DZDBZ is distorted octahedral symmetry. The value of D is relatively huge than found for normal Mn(II) complexes. In order to classify the position of the Mn in DZDBZ, the direction cosines of various Zn-O bonds have been calculated from X-ray data (assuming similar structure for DZDBZ) and given in Table 4 it shows the direction cosines of g/A values is matches with direction cosines Zn-O(2) was obtained from crystallographic data, it indicates that the paramagnetic transition metal ion namely Mn(II) ion present in the lattice substitutionally in place of zinc. The road maps simulated for two planes and agree well with the experimental one. The spin Hamiltonian parameters observed from single crystal analysis are further confirmed by taking polycrystalline EPR spectrum. The powder EPR spectrum of Mn(II)/DZDZB is shown in Fig. 8. The calculated spin Hamiltonian parameters are: $g = 2.0078$, $A = 9.6$ and $D = 52.24$ mT. These values are almost close to those parameters acquired from single crystal analysis. The powder EPR spectrum is simulated using these values which confirm the accuracy of the evaluated spin Hamiltonian parameters is shown in Fig. 8. The spin Hamiltonian parameters obtained for Mn(II) doped DZDZB are summarized in Table. 4. These values are good agreement with literature values [16-19]

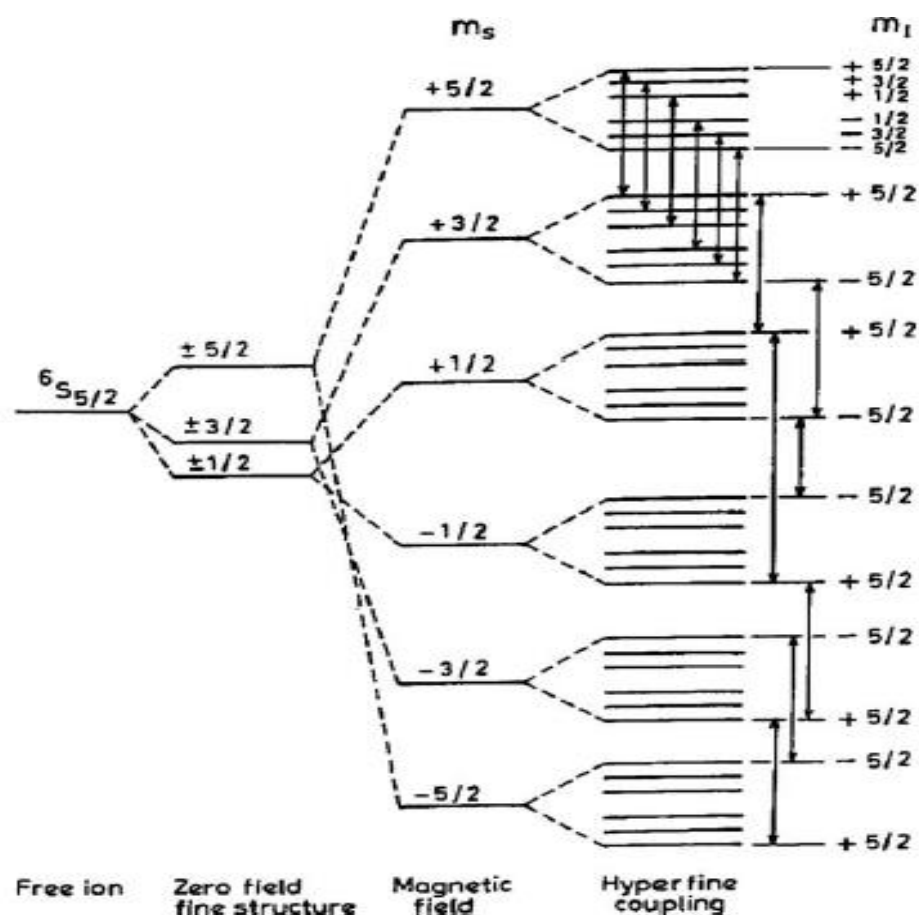


Fig 5: The schematic energy level diagram for $Mn(II)$ ion showing electronic levels in zero and strong magnetic fields together with splitting due to nuclear spin. In the present work, the hyperfine structure (hfs) observed at $g = 2.0$ at room temperature.

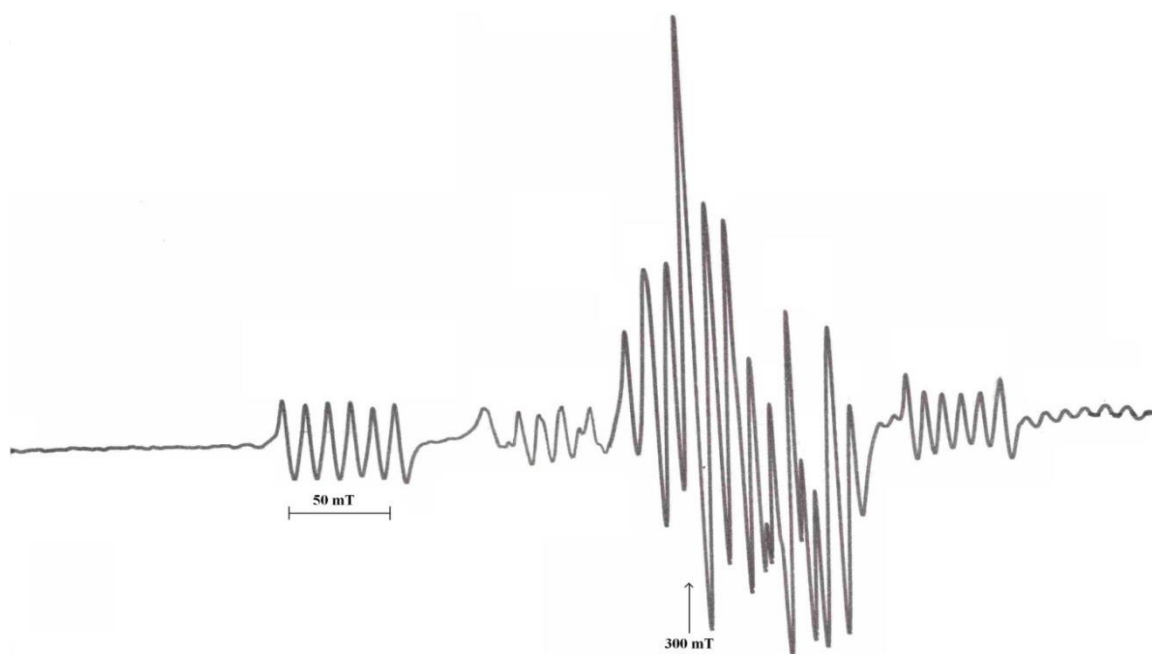


Fig. 6a: Single crystal EPR spectrum of Mn(II) doped DZDBZ, when B is parallel to axis c^* .
Frequency = 9.05508 GHz.

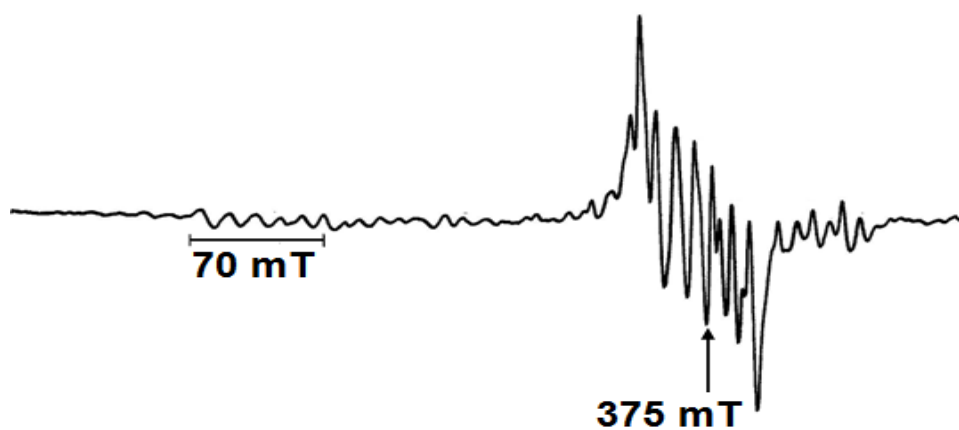


Fig. 6b: Single crystal EPR spectrum of Mn(II) doped DZDBZ, when B is parallel to axis b.
Frequency = 9.05859 GHz.

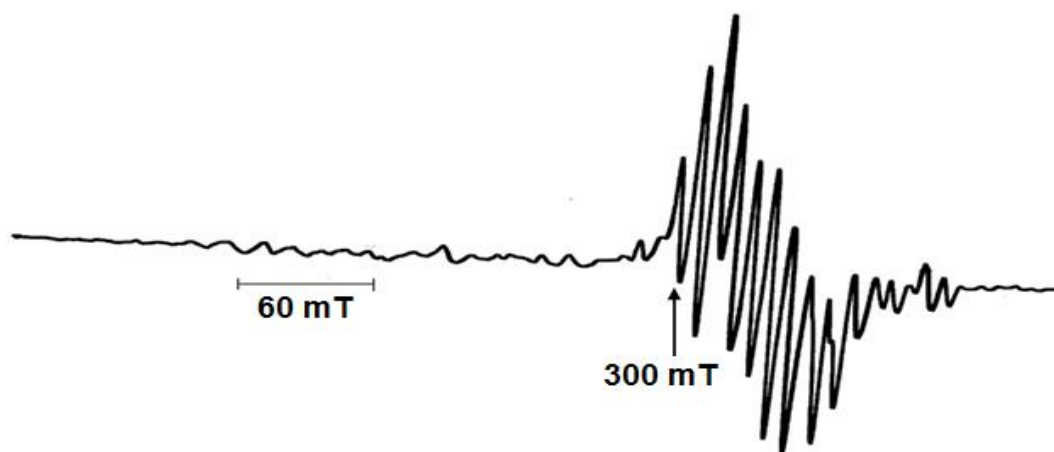


Fig. 6c: Single crystal EPR spectrum of Mn(II) doped DZDBZ, when the applied magnetic field (B) is parallel to axis a. Frequency = 9.05911 GHz.

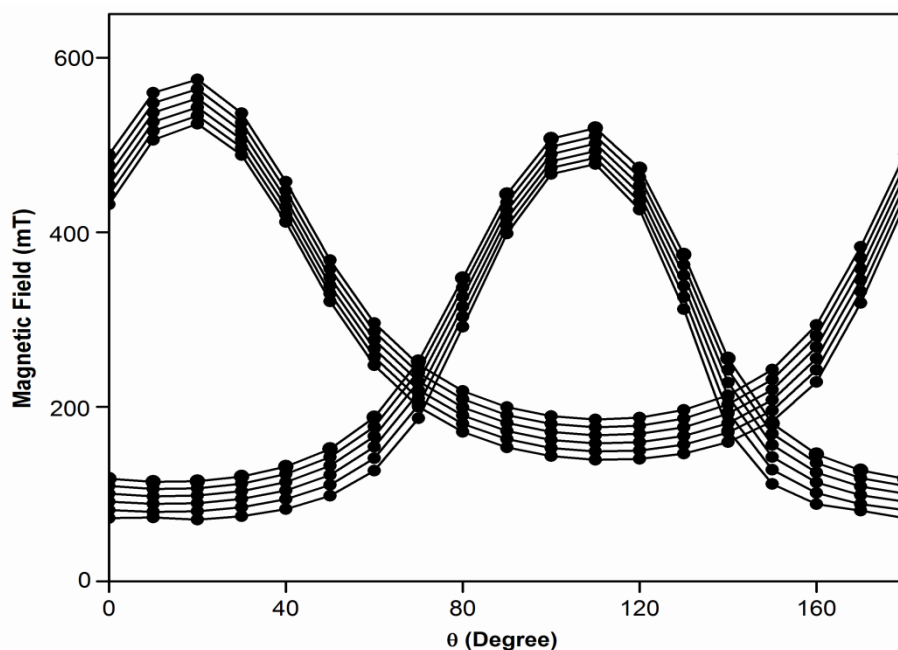


Fig. 7a: Angular variation plot of Mn(II) doped DZDBZ in the ac^* plane. Frequency = 9.05869 GHz. Here and Fig.4b, solid circles represents to experimental points, whereas solid lines are theoretically calculated. Here $\pm 5/2 \leftrightarrow \pm 3/2$ transition only shown because $\pm 3/2 \leftrightarrow \pm 1/2$ and $+1/2 \leftrightarrow -1/2$ transitions were difficult to follow due to overlap of the intermediate transitions with the transitions of other site.

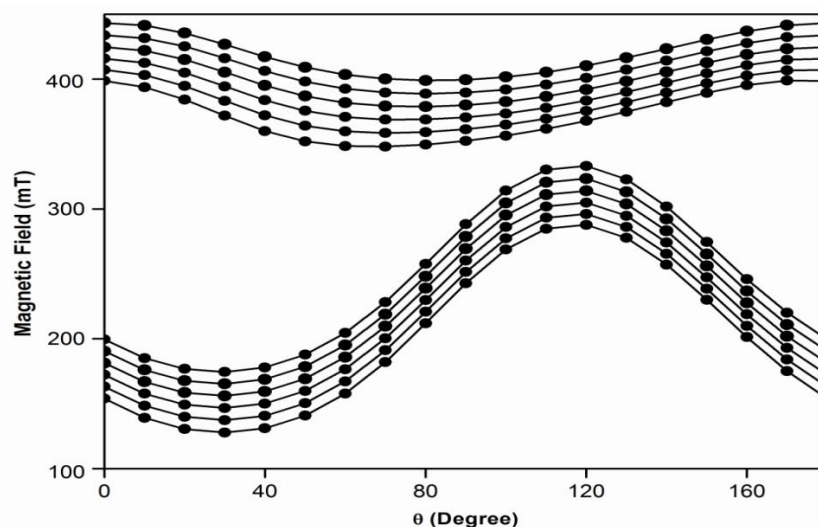


Fig. 7b: Angular variation plot of Mn(II) doped DZDBZ in the ab plane. Frequency = 9.05911 GHz.

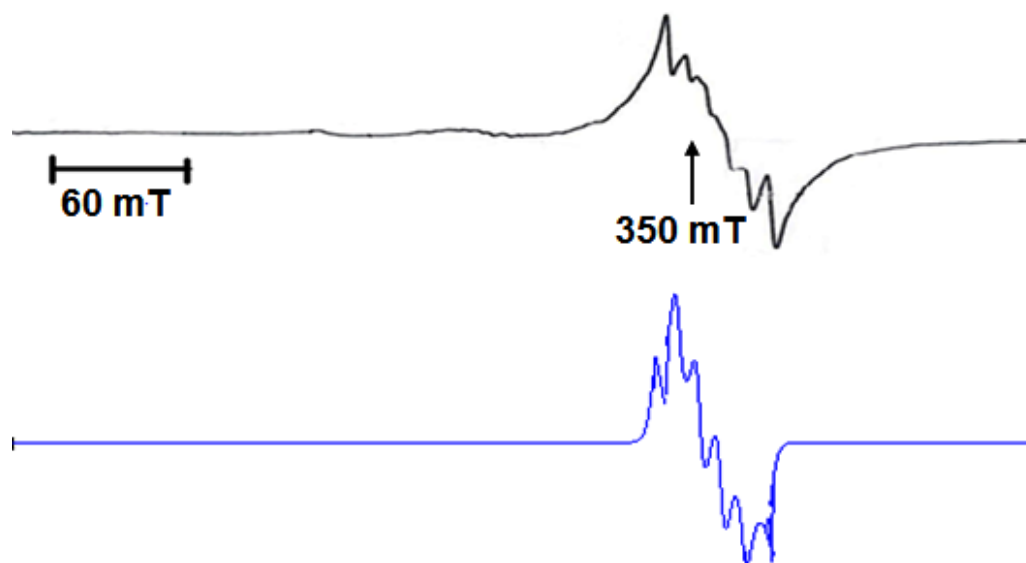


Fig. 8: EPR spectrum of powder sample of Mn(II) doped DZDBZ at room temperature (top) whereas the bottom one corresponds to simulated spectrum using SimFonia program. Frequency = 9.06871 GHz.

g matrix	Principle values			Direction cosines		
				a	b	c*
2.028	0.001	0.020	1.997	-0.7082	0.2216	0.6808
	1.992	0.001	2.004	-0.5816	0.7012	0.4126
		2.012	2.008	-0.3596	0.6795	0.6471
A matrix (mT)						
8.35	-0.10	0.14	8.32	-0.7192	0.2336	0.6542
	8.67	-0.38	8.54	0.5948	0.6936	0.4062
		9.55	9.74	0.3588	0.6813	-0.6379
D matrix (mT)						
23.1	7.3	-19.5	35.4	0.8192	0.2488	0.5184
	10.1	-16.3	7.46	-0.4590	0.8516	0.2529
		-33.2	-42.85	-0.3724	0.0306	0.9344

Table.3: The spin Hamiltonian parameters obtained from the single crystal rotation for the Mn(II) doped DZDBZ using program EPR-NMR [15]

M-L bond	Direction cosines		
	A	B	c
Zn(1)-O(1)	-0.3139	0.6504	0.6919
Zn(1)-O(1) _w	0.4338	0.0289	-0.9014
Zn(2)-O(2)	0.8301	0.1035	0.5493
Zn(2)-O(2) _w	0.3482	0.0078	-0.9350

Table 4: The direction cosines of Zn -O obtained from the crystallographic data.

4d. Position of the Mn(II) ion in DZDBZ

The crystal structure of Diaquazinc(diaquabismalonato)zincate (DZDBZ) is belongs to monoclinic with space group C2/m and containing two atoms per unit cell (see Fig.1a). In this structure, both the zinc atoms are six coordination with slightly distorted octahedral geometry. Coordinated water molecule in the apical position and four oxygen atom from two [at Zn(1)] and four [at (Zn(2))] malonato ligand in the equatorial plane, they have familiar occurrence for syn-anti geometry. The $3d^5$ ion with $s = 5/2$ and $I = 5/2$ exhibits thirty hyperfine lines from a single crystal. Mn⁺² may be entered into the lattice by substitutionally or interstitially. The direction cosines of the Zn-O_w and Zn-O_m (w-water, m-malonato) bonds obtained from single crystal XRD are tabulated in Table 4. The direction cosines of principle g and A values are almost matches with the direction

cosines of Zn(1)-O_w(1) bond of DZDBZ. The deviation between the directions was around 5. This reveals that the impurity has entered the lattice in substitutional position. The ionic radii of Zn (0.074 nm) is being smaller as compared to Mn (0.089 nm), therefore the manganese ion fits to enter the lattice substitutionally.

4e. Covalency of metal ligand bonds

The covalency of the bond between manganese and oxygen's ligand can be calculated using Matumura's plot. The covalency of a bond between manganese and its ligands depends on the magnitude of the isotropic hyperfine coupling constant "A". An approximate relationship for the covalency of a bond between the atom p and q and their electro negativities χ_p and χ_q is given.

$$C = [1 - 0.16(\chi_p - \chi_q) - 0.035(\chi_p - \chi_q)^2] / n$$

Here, n is the number of neighboring atoms surrounding the Mn(II) ion. Using the values $\chi_{Mn} = 1.55$ and $\chi_O = 3.44$, (Pauling's scale) and the percentage of covalency obtained for our case using the above equation is 8.5%, indicating that compound was almost ionic nature. Also, the covalency of the bond between manganese and its ligands will influence the magnitude of the isotropic hyperfine coupling constant. The hyperfine coupling constant A obtained from Matamoras's plot matched well with the calculated value.

5. CONCLUSION

Homobimetallic zinc malonato complex have been synthesized. The structure of the complex have been confirms by single crystal XRD and FT-IR. Homobimetallic zinc malonate complexes have selected as good diamagnetic host lattice to incorporate Mn(II) has dopant. Single crystal rotations have been performing three orthogonal planes carried out room temperature. EPR spectra of Mn(II) doped DBDBZ have been studied at laboratory temperature. The EPR magnetic tensor parameter g, A, D, E have been obtained from single crystal rotation in three orthogonal planes. The location of the Mn(II) present in the host lattice substitutionally in place of zinc(II) ion. The magnitude of the hyperfine splitting constant A indicates that the bonding between paramagnetic ion and the ligands are ionic nature. The large D and E values reveals that distortion present in the crystal lattice due to steric effect of the crystal packing caused by dicarboxylic acid ligand. The optical spectrum have helped to calculate crystal field splitting parameter Dq and Racah interelectronic repulsion parameters B and C also have been evaluated. FT-IR and powder XRD are assisting to reconfirm the molecular structure of DBDBZ.

ACKNOWLEDGEMENTS

The authors thanks to University Grand Commission [33-316/2007(2007)] for financial assistance.

REFERENCES

- [1] Parthipan. K, Ramachitra. S, Rao. P.S, (2014), "Structural evaluation and position of the VO^{2+} in diaaquacadmium(diaaquabismalonato)cadmate: spectroscopic studies", *Monatsh Chem.* 2014; 145: 585-592.
- [2] Parthipan. K, Rao. P.S, (2010), "Molecular structural identification and position of Cu(II) ion Diaqua(2,2'-bipyridinemalonatozinc(II): spectroscopic studies: spectroscopic studies", *J..Mol.Struct.*2010; 977: 130-136.
- [3] Ruiz-Perez. C, Sanchiz. J , Molina.M. H, Lloret. F, Julve.M, (2000), " Synthesis, crystal structure and magnetic properties o the malonate bridged bimetallic chain $[\text{Mn(II)Cu(II)(mal)}_2(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$ " *Inorg. Chim. Acta.* 2000; 298: 202-208.
- [4] Sain. S, Maji. K. T, Mostafa. G , Lu. T. H, Chaudhuri N. R , (2003), "Two new supramolecular malonato complexes of manganese (II) ; Synthesis, crystal structure and magnetic property" *Inorg. Chim. Acta.* 2003; 351: 12-20. 746
- [5] Sapina.F, Escriva.E, Folgado.J.V, A. Beltran, Fuertes.A, Drillon. M , (1992), " A new magnetic lattice in the cdta family structure and magnetic properties of the novel homo and heterometallic chain $\text{Cu}[\text{M}(\text{cdta})]_2(\text{NO}_3)_2 \cdot 15\text{H}_2\text{O}$ " *Inorg. Chem.* 1992; 31: 3851-3858.
- [6] Brandstetter. H., Engh. R. A, Roedern. E. G. V, Moroder. L, Huber. R, Bore.W, Grams.F , (1998) Structure of malonic acid based inhibitors bound to human neutrophil collagenase. A new binding model explains apparently anomalous data", *Protein Science.* 1998; 7: 1303-1309.
- [7] Gelasco. A, Baldwin. M, Pecoraro, Thorp. V. L(Eds) (1995) " A modeling Approach for understanding the Mechanism of Manganese Enzyme in Mechanistic Bioinorganic Chemistry" , *Adv. Chem Series , ACS books, Washington.*
- [8] Delgado. F.S, Molina. M. H, Sanchiz. J, Preez. C. R, Martin.Y.R, Lopez.T, Lloret. F and M. Julve, (2004), " Synthesis, crystal structure and magnetic property of two dimensional malonato bridged cobalt(II) and nickel(II) compound", *CrystEngComm.* 2004; 6: 106-111
- [9] F. S. Delgado, F. Lohas, F. Lloret M. Julve, C.R. Preez, (2008), Supramolecular networks in copper(II) malonate complexes, *Crystal Growth Design.* 2008; 8: 3219-3232.
- [10] Parthipan. K, Ramachitra. S, Rao. P.S, (2013), "Synthesis and characterization of Bimetallic malonatozinc (II) and copper doped complex ", *J. Applicable. Chem.* 2013; 2: 680-690.

- [11] Lever. A.B. P, (1986), “ Inorganic Electronic Spectroscopy ” 2nd ed., Elsevier, New York.
- [12] Nakamoto.K, (1986), ‘Infrared and Raman Spectra of Inorganic and coordination compounds’’1986 ; 4th edition, Wiley Interscience, Newyork.
- [13] Abragam. A, Bleaney. B, (1970), “Electron Paramagnet Resonance of Transition metal Ions”, Clarendon Press, Oxford.
- [14] Pilbrow. J.R , (1990) “Transition ion Electron Paramagnetic Resonance”,1990; Clarendon Press, Oxford.
- [15] Clark.F, Dickson. R.S, Fulton. D. B, Isoya. J, Lent.A, McGavin. D. G, Mombourquette. M. J , Nuttall. R. H. D, Rao. P. S, Rinnerberg. H, Tennant. W.C, Weil. J. A, (1996), EPR –NMR program, 1996 ; University of Saskatchewan, Saskatoon, Canada
- [16] Sangita. P, Kripal. R, (2012), “ Zero field splitting parameters of Mn^{2+} in Bis (L-asparaginato) Zn (II) at interstitial orthorhombic symmetry site”, Spectrochim Acta. 2012; 91(A49): 290-294.
- [17] Ramachitra. S, Ramesh.H, Muthuausteria. P, Parthipan. K, (2014), “Structural elucidation and location of Mn(II)ion in Tetraaquabis(hydrogen maleato)cadmium(II): single crystal EPR studies ”, J..Mol.Struct. 2014; 1058: 173-180.
- [18] Boobalan. S , Rao. P.S , (2010), Structural Elucidation of Transition metal complexes by single crystal EPR study J. Organo. Chem. 2010; 695 963-969.
- [19] Natarajan.B, Mithira. S, Rao. P. S, (2008), “Identification of symmetry, sstructure and defects of dopant Mn(II) ions in $Zn(C_3H_3O_4)_2(H_2O)_2$ by Single crystal EPR technique”, Solid State Science. 2008; 10 1916-1923.