Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2013, 2 (3): 680-690

(International Peer Reviewed Journal)

Synthesis and Structural Characterization of Bimetallic malonatoZinc(II) and its Copper(II) doped Complex

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Received on 19th March and finalized on 15th May 2013.

ABSTRACT

The crystal structure of Zinc(II) malonato$[Zn(H_2O)_2(Zn(mal)_2(H_2O)_2]_n$ *complex has been investigated by X-ray diffraction technique. Electron paramagnetic resonance, optical, FTIR and powder XRD studies have been carried out on Cu(II) doped Zinc(II) malonato complex to get information about the effect of dopant. Angular variation of copper hyperfine lines in EPR study shows the presence of a single site with g and A values as:* $g_{xx} = 2.101$, $g_{yy} = 2.068$, $g_{zz} = 2.365$ *and* $A_{xx} = 4.32$ *mT,* $A_{yy} = 3.55$ *mT,* $A_{zz} = 12.60$ *mT. The direction cosines of principle g and A values suggest that electric field around the impurity is rhombic and it is present substitutionally through metal carboxylate oxygen bond of the host lattice. The low value of* $A_{\parallel}$ *has been explained by taking account of considerable admixture between the ground and excited states of copper (II) such as* $d_{x^2-y^2}$ *and* d_{z^2}*, with admixture coefficients of* $a = 0.144$, $b = 0.988$, $c = 0.052$, $d = 0.019$ *and* $e = -0.019$*, where coefficients a and b correspond to coefficients for* d_{z^2} *and* $d_{x^2-y^2}$ *orbitals respectively. Few other calculated parameters such as* $\kappa = 0.37$, $P = 290 X 10^{-4}$ cm^{-1}; $\alpha = 0.88$ *and* $\alpha' = 0.53$ *indicate considerable covalence.*

Keywords: Bimetallic zinc, malonato, copper, admixture coefficient, EPR, optical.

INTRODUCTION

Some of the fundamental questions in molecular biology are how proteins fold and how do the molecules assemble in multi-molecular units. Measuring the distance between the sites in protein or a molecule is an ultimate choice to answer these questions. EPR provides an opportunity to measure distance between paramagnetic sites due to the large magnetic moment of electrons. Electron spin relaxation is an important phenomenon in EPR that has wide range of applications including measuring distance [1] in proteins and macromolecules. There are many enzymes and proteins found in biological systems in which Cu(II) is an active centres [2-5]. So understanding of Cu(II) by EPR is significant [6-8]. EPR of Cu(II) complexes have been broadly studied because Cu(II) can exist in several geometries viz., octahedral, tetrahedral, square planar and square pyramidal [9-14]. Dicarboxylic acid compounds are an essential components for living organisms and have strong coordination ability for various transition metal ions such as Cu(II), Co(II), Ni(II) etc. Malonic acid has very fascinated interest because of its two carboxylic groups, which can accept various coordination modes such as anti-anti, syn-anti or syn-syn, and thereby it is useful for making molecular magnets. Transition metal containing malonate complexes are very useful in various fields of chemistry, comprise synthetic, theoretical, crystal engineering, material chemistry and also results are very attractive and diversified Some of malonate complexes have, potential application as magnet, optical, catalyst material, absorbent, polymorphs and biologically active compounds [15-18]. 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 [19-22]. Transition metal ion doped crystals are useful for laser and optical fiber applications because of their spectroscopic behaviors. Based on the above fascinating phenomenon, homobimetallic zinc complex - Diaquazinc(diaquabismalonato)zinc(II) (here after abbreviated as DZDBZ)using malonic acid as chelating ligand has been synthesized and its structure has been characterized by single crystal X-ray diffraction and above mentioned complex act as an excellent diamagnetic host for introducing paramagnetic ion particularly copper ion (d^9) to calculate spin Hamiltonian parameters of Cu(II), find out position whether Cu(II) ion enters the lattice as interstitially or substitutionally and also to have better understanding of the physical nature of the bonding in the system. The study is further extending to calculate different molecular orbital parameters and nature of bonding involving the metal ion with ligands. Generally, paramagnetic impurity Cu(II) have entered into various zinc malonato complexes interstitially[23-25]. Some of interesting observation occur for present case, paramagnetic impurity Cu(II) has been entered substitutionally, which is favourable due to carboxylate oxygen chelating part.

MATERIALS AND METHODS

Synthesis of $[Zn(H_2O)_2(Zn(mal)_2(H_2O)_2]$ and Cu(II) doped $[Zn(H_2O)_2(Zn(mal)_2(H_2O)_2]$: 1.144 g of malonic acid (11 mmol) and 2.666 g of zinc acetate (10 mmol) were dissolved in 100 mL of water. The solution was stirred, heated on water bath to evaporate acetic acid. Solution kept for crystal growth. After couple of weeks, good and well shaped crystals of DZDBZ were separated out from solution. DZDBZ crystals were dissolved in water and then 0.1% by weight of $CuSO_4$ was added as dopant. Good and well shapedCu(II) doped DZDBZ crystals were obtained after 20 days.

X-ray Crystallography: Single crystal of the complex Diaquazinc(diaquabismalonato)zinc(II) (DZDBZ) was mounted on an Oxford Diffraction Xcaliburdiffractometer with an Eos (Nova) detector consists of ω and φ scan modes. The data collection was performed on a Bruker APEX2 CCD area-detector diffractometer employing graphite-monochromatizedMo Kα radiation (λ = 0.71073 Å). The data reductions were processed with SAINT [26] software. The structure was solved by the direct method using SHELXS-97 [27]and is refined on F^2 by fullmatrix least-squares technique using the SHELXL-97[28] program package. All H atoms are fixed geometrically and allowed to ride on their parent C atoms, with C—H distances fixed in the range 0.93–0.97 Å. The H atom displacement parameters were restricted to be Ueq of the parent atom. Table 1 lists crystallographic details.

Physical measurements: EPR spectra were recorded at room temperature on a JEOL JES-TE100 ESR spectrometer operating at X-band frequencies, having a 100 kHz field modulation to obtain the first derivative EPR spectrum. DPPH was used as the standard for magnetic field correction of g-factor calculations. Angular variation was made at room temperature by rotating the crystal along the three mutually orthogonal axes a, b, c* in 10º interval. Isofrequency plots of each plane were simulated using program EPR-NMR [29]. The EPR spectrum of powder sample was simulated using SimFonia program developed andsupported by BrukerBiospin. Optical spectrum of copper doped DZDBZ was recorded at room temperature using a Varian Cary 5000 Ultraviolet (UV-Visible) near infrared spectrophotometer in the region of 200-1200 nm**.** In the present study, the FTIR spectrawasrecorded on a Shimadzu FTIR - 8300/8700 spectrometer, 4 cm^{-1} resolution, automatic gain, 20 scan, in the region of 4000-400 cm^{-1} at RT . The measurements were made using almost transparent KBr pellets containing fine powder sample at room temperature. In the crystalline material, the powder X-ray diffraction (XRD) was used to identify and characterize the powder sample possessing a long and shot range order respectively. In the present investigation, powder XRD were carried out for doped and undoped materials on a Analytical X'Pert Pro diffractometer with Cu Kα radiation of wavelength 0.15406 nm and 2θ values of 5and 75°.

Table-1: Crystal data and structure refinement for DZDBZ$[[Zn(H_2O)_2(Zn(mal)_2(H_2O)_2]_n$

Empirical formula	$C_6H_{12}O_{12}Zn_2$	Θ-range for data collection	3.21 to 25°
Formula weight	406.90	Index ranges	$-6 \leq h \leq 8$
Temperature	293(2)K		$-5 \leq k \leq 8$
Wavelength	0.71073Å		$-13 \leq l \leq 12$
Crystal system	Monoclinic	Reflections collected	1942
Space group	$P2_1/n$	Independent reflections	1052 [$R_{(int)}$ = 0.0112]
a/b/c(Å)	7.305(4);7.412(4);11.075(7)	Refinement method	Full-matrix least-squares on F^2
α/β/ γ(°)	90;95.36(5);90	Data / restraints / parameters	1052 / 0 / 79
Volume	597.12(6) $Å^3$	Goodness-of-fit on F^2	1.219
Z	2	Final R-indices [I>2σ(I)]	R_1 = 0.0357, wR_2 = 0.1299
Density (calculated)	2.263μg/m^3	R-indices (all data)	R_1 = 0.0522, wR_2 = 0.1386
F(000)	408	Extinction coefficient	0.061(5)
Crystal size	0.20 x 0.20 x 0.19 mm^3		

RESULTS AND DISCUSSION

Description of Crystal Structure: The title compound, $C_6H_{12}O_{12}Zn_2$ (DZDBZ), crystallizes in monoclinic with space group $P2_1/n$ with one molecule in the asymmetric unit. The obtained cell parameters are a=0.7305(4), b= 0.7412 (4), c = 1.1075 (7) nm: β = 95.364(5)˚, α, γ = 90˚ and V = 597.12(6) $Å^3$. The structure is solved by direct methods procedure using SHELXS-97 and refined by SHELXL-97 with full matrix least-squares technique to a final R- factor of 0.030. In order to obtain detailed information on molecular conformations in the solid state, X-ray studies of the title compound (DZDBZ) have been carried out at room temperature. X-Ray analysis confirms the molecular structure and atom connectivity for DZDBZ as illustrated in figs. 1&2. The bond distances and bond angles of DZDBZ are comparable matched with cobalt and nickel malonato complexes. The central zinc atom lies in an inversion center (fig. 1). 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 bidentatemalonate 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.

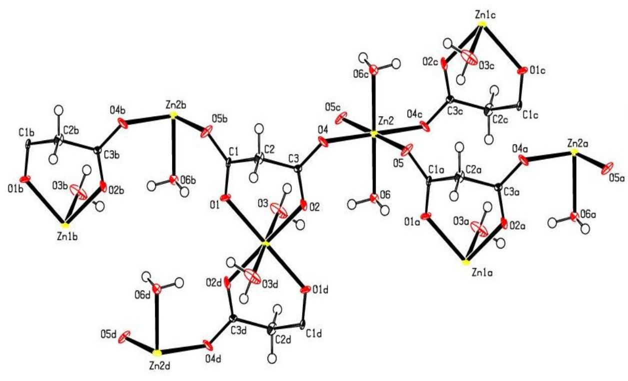
Table-2: Selected bond lengths (Å) for DZDBZ

Zn(1)-O(1)	2.047(3)
Zn(1)-O(2)	2.051(3)
Zn(1)-O(3)	2.153(3)
Zn(2)-O(6)	2.086(2)
Zn(2)-O(4)	2.138(3)
Zn(2)-O(5)	2.153(3)

Table-3: Selected Bond angles (°) for DZDBZ

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

All the bond angles around Zn are close to 90°. 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. Some of the important bond lengths are listed in Table-2 and bond angles are listed in Table-3. 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 [30-33]. Two water molecules and fourcoordinated 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, [34] as follows: q_2=0.443(3) Å, φ =359.6(5) °, Δ_s(C2) = 0.5(4), in which only the methylene group is significantly displaced from the chelating six-membered chelate.



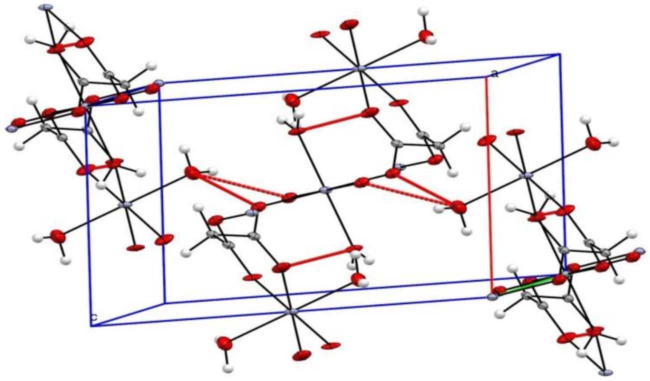


Figure-1: The molecular structure of $[Zn(H_2O)_2(Zn(mal)_2(H_2O)_2]_n$. **Figure-2:** The packing diagram for DZDBZ along b-axis in a crystal.

This ligand adopts envelope conformation, with the puckering parameters q_2 and φ and the smallest displacement asymmetric parameters, Δ_s, [34] as follows: q_2=0.443(3) Å, φ =359.6(5) °, Δ_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 vanderwals interactions, the crystal packing is stabilized by O-H…O hydrogen bonds forming a three dimensional network.

Optical absorption studies of Cu(II) doped DZDBZ: Copper(II) ion has d^9 configuration with ^2D ground state. The broad adsorption band observed is due to the transition between the levels ^{2}Eg and $^2T_{2g}$. The d^9 electronic configuration of this ion gives three electrons in the two degenerate e_g orbitals leading to a doubly-degenerate electronic ground state which causes distortion in the octahedral symmetry. In tetragonal distorted octahedral symmetry (C_4v), ^2E_g splits into $^2B_{1g}$ (corresponding to dx^2- y^2) and $^2A_{1g}$ (corresponding to dz^2) while $^2T_{2g}$ splits into $^2B_{2g}$ (corresponding to d_{xy}) and ^2E_g (corresponding to $d_{xz,}$ d_{yz}). The optical adsorption spectrum of Cu(II)/DZDBZ recorded at room temperature is shown in fig. 3.

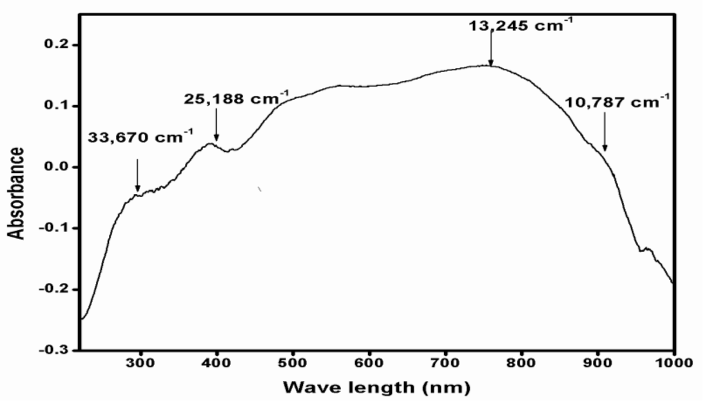


Figure-3: Optical absorption spectrum of Cu(II)/DZDBZ.

It shows four characteristic bands at 297, 397, 755 and 927 nm. The band at 297 nm is due to charge transfer band and remainingthree are d-d transition bands. The distortion is attributed only to tetragonal and not to any other lower symmetry. Accordingly, the bands are arributed to the transitions $^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$, respectively. The crystal field stabilization energy parameters D_q, D_t and D_s are calculated with help of the following equations [35]

$^2B_{1g} \rightarrow {}^2E_g \rightarrow E1 = 10Dq + 3Ds- 5Dt$

$^2B_{1g} \rightarrow {}^2B_{2g} \rightarrow E2 = 10Dq$

$^2B_{1g} \rightarrow {}^2A_{1g} \rightarrow E3 = 4Ds + 5Dt$

Parameters thus, evaluated are: Dq =1324, Ds = 1156 and Dt = 1232 cm^{-1}

The crystal field parameters confirm a tetragonal distortion for copper ion in the DZDBZ lattice.

FITR and powder XRD studies: The IR spectrum of DZDBZ and Cu(II) doped DZDBZ was recorded at room temperature and it is shown in fig. 4. The band observed at 1588 cm^{-1} was assigned to carboxylate (COO^-) symmetrical stretching and the bands appeared at 3246 and 3105 cm^{-1} were assigned to O-H bending of water ligand. Three bands were observed at 965, 781 and 732 cm^{-1} corresponds to bending modes of O-C-O bond. The band observed at 1445 was assigned to C=C stretching. The bands observed at 1184 and 2851 cm^{-1} were assigned to $–CH_2$ (bending) and symmetry stretching.

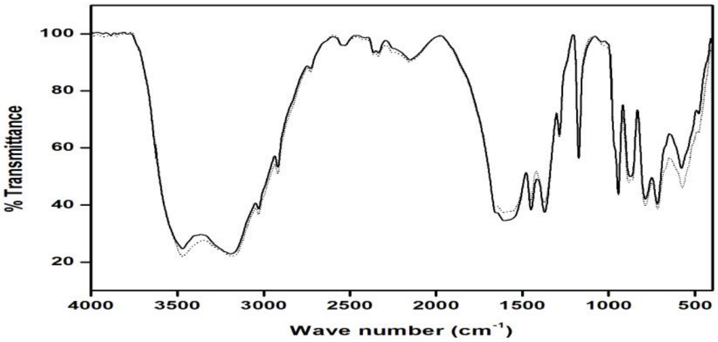


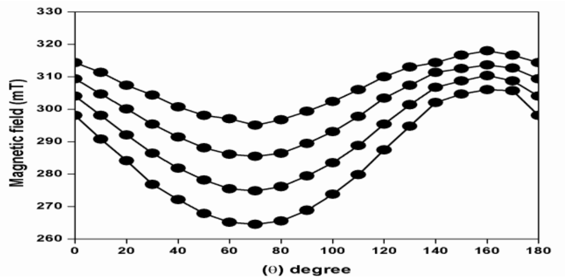
Figure-4:FT-IR spectra of pure (top) andCu(II) doped DZDBZ (bottom) at room temperature

Table-4: The calculated lattice parameters of DZDBZ and Cu(II)-doped DZDBZ from powder XRD, along with single crystal XRD of DZDBZ.

Lattice parameters(nm) of DZDBZ	**Lattice parameters (nm) from powder XRD**	
From Single crystal XRD	DZDBZ	Cu(II)/DZDBZ
a = 0.7306	a = 0. 7180	a = 0.7208
b = 0.7412	b = 0.7514	b = 0.7571
c =1.1075	c = 1.1102	c = 1.1123

The powder XRD spectrum of DZDBZ and copper doped DZDBZ recorded at room temperature. Lattice parameters have been calculated from powder XRD pattern for Cu(II) and DZDBZ and given in table 4 along with single crystal data of DZDBZ. These results specify that after doped Cu(II) ion, the structure of host lattice never changed due to low concentration of impurity.

EPR studies: The EPR spectra were recorded by rotating the suitable sized crystal in the magnetic field about the three mutually perpendicular axes a, b, c* for every 10º interval. Single crystal EPR of Cu(II) ion doped DZDBZ furnish to four EPR hyperfine lines resultant to S = 1/2 and I = 3/2 with allowed transitions $\Delta M_s = \pm 1$ and $\Delta M_I = 0$. During crystal rotations four EPR transition were observed for all the three planes, it indicates a single magnetically distinctive copper ion present in the lattice even through unit cell contain two molecules (Z =2). The shape of four lines is not identical to one another, because of overlapping of lines corresponding to copper isotopes Cu^{63} and Cu^{65}. The angular variation of the spectra studied at every ten degree orientation of the crystal in the magnetic filed in three mutually perpendicular planes are illustrated in figs. 5-7. In these figures solid circle correspond to the experimental points whereas a continuous straight line corresponds to simulated points. A good agreement is obtained between two.



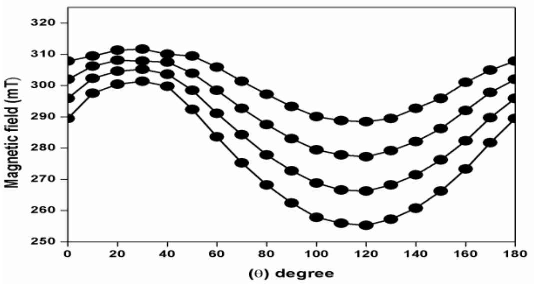


Figure-5: Angular variation plot of Cu(II)/DZDBZ **Figure-6:**Angular variation plot of Cu(II)/DZDBZ single crystal in the ac* plane, ν = 9.06856 GHz.single crystal in the bc* plane,ν = 9.06849 GHz.

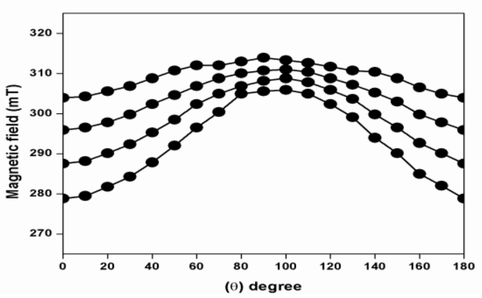


Figure-7: Angular variation plot of Cu(II) /DZDBZ single crystal in the ab plane, ν = 9.07754 GHz

Calculation of Spin Hamiltonian parameters: In order to extract the principal values of the magnetic tensor, the variations of the hyperfine features of copper are followed in the three planes ab, bc*and ac*. Cu(II) ion has a $3d^9$ configuration with S = 1/2 and I = 3/2 respectively. These EPR spectras of all three planes were obviously fitted to the following spin Hamiltonian parameters.

$\mathcal{H}s = g_{xx}\beta B_x S_x + g_{yy}\beta B_y S_y + g_{zz}\beta B_z S_z + A_{xx} S_x I_x + A_{yy} S_y I_y + A_{zz} S_z I_z.$

It includes only electron Zeeman and hyperfine interactions. The quadruple and nuclear Zeeman have been ignored. The spin orbit interaction is intrinsic in g value, g and A tensors are constructed and diagonalised to find out principle values. By making use of program EPR-NMR [29], the spin Hamiltonian parameters have been calculated using the angular variation plots and the results are shown in Table 5 along with respective directions cosines. The spin Hamiltonian parameters obtained for Cu(II)/DZDBZ are correlated with the results obtained from some other works [23,25,36-38]. The spin Hamiltonian parameters g and A tensor reveal that crystalline electric field around the Cu(II) ion is orthorhombic symmetry. The direction cosines of principal g and A values are close to each other signifying that the tensors are coexisting, which further established by having the maxima and minima at the same angle in the isofrequency plots in all the three planes.

Table-5: Spin Hamiltonian Parameters obtained from the single crystal rotations for Cu(II) in DZDBZ using programEPR-NMR [29].

Principle values				**Direction cosines**		
				a	b	c*
g-matrix						
2.137	-0.046	0.080	2.101	-0.3677	0.5624	0.7405
	2.172	0.124	2.068	0.8414	0.5403	0.6259
		2.231	2.365	-0.3950	0.6259	-0.6719
A matrix (mT)						
5.88	-1.89	-2.64	4.32	-0.4348	0.5171	0.7371
	6.04	3.51	3.55	0.8993	0.2077	0.3848
		8.58	12.60	0.0458	0.8303	-0.5553

According to the principle values of g tensors**,** the g values are in the $g_{zz} > g_{xx} > g_{yy}$ order. These values are drive use to comment on the state of the unpaired electron, when the ratio $R = (g_{xx} - g_{yy}) / (g_{zz} - g_{xx})$ less than unity, it means that the unpaired electron is dominantly in the dx^2-y^2 state and when R is the greater than unity, the unpaired electron is in the dz^2 state. The obtained value of R in the present case is R = 0.11, it is clearly says that dx^2-y^2 is ground state. It is possible to compare the direction cosines of the metal ligands (Zn-L) calculated from X-ray crystallographic data and direction cosines of principal g and A values, to provide ideas about position of dopant. In the interest of locating the impurity site in the Cu(II)/DZDBZ, we have analyzed crystal structure of DZDBZ depicted Fig. 1. DZDBZ possesses two molecules (Z =2) under the space group $P2_1/n$. Both zinc atoms are coordinated with six coordinate in slightly distorted octahedral environments, they have in common the occurrence of two trans water coordinated water molecule in the apical position and four oxygen atom from two[at M(1)]and four [at (M(2)] malonato ligand in the equatorial plane. The $3d^9$ ion with s =1/2 and I = 3/2 exhibits four line hyperfine pattern from a single crystal. Cu(II) may entered in the lattice DZDBZ either by substitutionally or interstitially. In order to substantiate, the direction cosines of the Zn-L (L = oxygen atoms derived from malonato anion and water molecules) bonds have been calculated from crystallographic data of DZDBZ and are given in Table 6.

Table-6: The direction cosines of Zn -O, obtained from the crystallographic data.

M-L bond	**Direction cosines**		
	a	b	c*
Zn(1)-O(1)	-0.3139	0.6504	0.6919
Zn(1)-O(2)	0.8301	0.1035	0.5493
Zn(1)-O(3)	0.4338	0.0289	-0.9014
Zn(2)-O(4)	-0.0526	0.5248	0.8948
Zn(2)-O(5)	0.4918	0.0735	-0.1038
Zn(2)-O(6)	0.3482	0.0078	-0.9350

The direction cosines of principle g and A value when matched with the direction cosines of metal - ligand bonds, one of them is almost matched, which suggested that the impurity has entered the lattice in substitutional position. The ionic radius of Zn(II) and Cu(II) are 0.075 nm and 0.073 nm respectively. Because of the small ionic radius of Zn(II) as compared with Cu(II) seems fit to enter the lattice substitutionally in place of zinc. In the present case direction cosines of g/A values is close almost matches with the direction cosines of Zn(1)-O(1) were obtained from crystallographic data is suggested that the paramagnetic impurity is present in the lattice substitutionally.

Polycrystalline spectra of Cu(II)/DZDBZ: Polycrystalline EPR spectrum of Cu(II)/DZDBZ is recorded at laboratory temperature and is given in Fig. 8. The spin Hamiltonian parameters have been calculated using powder spectrum and the values are: $g_{\parallel}= 2.370$, $g_{\perp}= 2.080$. $A_{\parallel}$ =11.6 mT, and $A_{\perp}$ not resolved.

The spin Hamiltonian parameters (g and A) for powder Cu(II) doped DZDBZ are close to those observed from single crystal (Table 5). The parallel g value is greater than perpendicular one is representing that the ground state is $dx^{2}-y^{2}$. SimFonia program is used to simulate the powder spectrum and also given along with experimental one given in Fig. 8, where the good agreement has been found. Additionally the lowest values of $A_{\parallel}$ has explained by considering the admixture of $dx^{2}-y^{2}$ (ground state) with dz^{2}(exited state) orbital and metal ligand covalent nature.

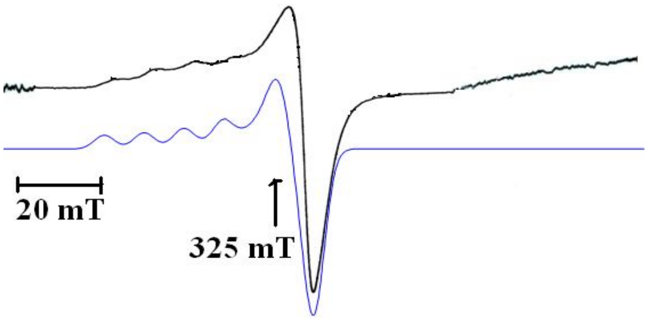


Figure-8: Poly crystallineEPR spectrum of Cu(II)/DZDBZ at room temperature (top) whereas the bottom one corresponds to simulated spectrum using SimFonia program.

Calculation of molecular orbital coefficients: The molecular orbital coefficient α^2 which gives a measure of covalent nature of σ-bonding, is given by the following expression [39]

$\alpha^2 = A_{\parallel}/0.036 + (g_{\parallel} - 2.0023) + 3/7\,(g_{\perp} - 2.0023) + 0.04$

Here, $g_{\perp}$is the average of g_{xx} and g_{yy}. Few more parameter such as α' can be evaluated from the normalization condition on the ground state orbital as $\alpha' = (1-\alpha^2)^{1/2}{}_{+}\,\alpha S$, where S is the overlap integral between the $d_{x^{2}-y^{2}}$orbital and normalized ligand orbital. The value of S is given as 0.076 for oxygen ligand. This complex found to be partially covalent nature. For Cu/DZDBZ the bonding parameters are, α^2= 0.78α =0.88 α'= 0.5276. The value of α^2 is unity if the bond between metal and the ligands is ionic and 0.5, if it is covalent. The present value 0.780 indicates partially covalent nature for the metal ligand bond. Additionally, we have calculated two more parameters namely P and κ using the below equation [40-42]

$A_{\parallel} = P\,[- (4\alpha^2/7) - \kappa + (g_{\parallel}-g_e) + 3/7\,(g_{\perp}-g_e)]$

$A_{\perp} = P\,[2\alpha^2/7) - \kappa + 11/14\,(g_{\perp}-ge)]$

Here, $P = 2\gamma Cu\beta\beta_n\langle r^{-3}\rangle$, γCu is the gyromagnetic ratio of copper, β is the Bohr magneton and β_n is the nuclear magneton, and κ is the dimension less hyperfine interaction constant [43]. The average of A_x and A_y is taken as $A_{\perp}$. From the above equations, P and κ have been evaluted and the values are ($\kappa = 0.369$, $P = 290X10^{-4}\ cm^{-1}$). The ratio of $P_{complex}$ to P_{free} ion is around 80%, indicating the delocalization of the d electron. The percentage of unpaired spin density on copper ion is 20% remaining density being distributed onto the ligands.

Determination of admixture coefficient: The spin Hamiltonian parameters show $d_{x^2-y^2}$ground state of the Cu(II) ion. The non axial symmetry of g and A tensor suggests a rhombic crystal field symmetry. Using g-values, the coefficient of the d-orbital of Kramer's doublet wave function for the ground state can expressed
$\Psi = a\phi_1\alpha + b\phi_3\alpha + ic\phi_2\alpha - id\phi_4\beta - e\phi_5\beta$
$\Psi^* = i\ (a\phi_1\beta + b\phi_3 - ic\phi_2 - id\phi_4 + e\phi_5\alpha)$
Where, $\phi_1 = d_{z^2}(A)$, $\phi_2 = d_{xy}\ (B_1)$, $\phi_3 = d_{x^2-y^2} \phi_4 = d_{yz}\ (B_3)$, $\phi 5 = d_{xz}(B_2)$. This equation represents that a =1, the system has d_{z^2}ground stateand lowest $A_{\|}$ value and if b =1, the system is in $d_{x^2-y^2}$and has the maximum hyperfine value. The term of admixture coefficient, the expression for the g and A values are given as [44]
$g_z = 2 - 4d^2 - 4e^2 + 8bc + 4de$
$g_x = 2 - 4c^2 - 4e^2 + 4\sqrt{3}ad - 4ce + 4bd$
$g_y = 2 - 4c^2 - 4d^2 + 4\sqrt{3}ae - 4be + 4cd$
$A_z = P\{8bc+4de+(6\xi-\kappa)(1-2d2-2e2)-3\xi[4c2+4b2-e2+\sqrt{(3)}a(d+e)+3(d-e)(c-b)]\}$
$A_y = P\{4\sqrt{(3)}ad-4ce+4bd+(6\xi-\kappa)(1-2c^2-2e^2)-3\xi[\sqrt{(3)}a+b)^2-c^2+4d^2-e^{2-}\sqrt{(3)}a(e+2c) +3dc-3be-3de]\}$
$A_x = P\ \{4\sqrt{(3)}ae-4dc-4be+(6\xi-\kappa)(1-2c^2-2d^2)-3\xi[\sqrt{(3)}a+b)^2-c^2-d^2+4e^{2-}\sqrt{(3)}a(d-2c) +3ce-3db+3de]\}$
Here a, b, c, d and e are the admixture coefficients of ϕ_1, ϕ_2, ϕ_3, ϕ_4 and ϕ_5 respectively. The ξ is a constant and depends on the electronic configuration of the ion and the values of 0.0952 for Cu(II) ion. Using the normalization condition and assuming e = -d, values of a, b, c and d are obtainedby iterative procedure. The coefficients, which gave the best fit to the observed g values are a = 0.144, b = 0.988, c = 0.052, d = 0.019 and e = -0.019. A comparison of these results reveals that there is considerable admixture of d-orbitals in the present compound.

APPLICATIONS

This Copper(II) doped homo bimetallic Zinc(II) complex is expected to be a non-linear optical material. Studies are underway.

CONCLUSIONS

In this work, we present the synthesis and spectroscopic properties of Bimetallic Zinc malonato complex Diaquazinc(diaquabismalonato)zinc(II) (DZDBZ) and its crystal structure has been determined by the X-ray diffraction method. The EPR and optical absorption spectra of the copper doped DZDBZ single crystal has been investigated. An FTIR and Powder XRD study confirms the studies host lattice in presence and absence copper ion. The angular variation of EPR spectra of single crystal Cu(II)/DZDBZ reveals copper(II) substituted in the host lattice. The spin Hamiltonian parameters g and A values have been evaluated. The ground state wave function coefficients obtained from spectral data indicate the mixing of $d_{x^2-y^2}$and d_{z^2} orbitals. From the optical data, the crystal field parameter and the tetragonal parameters have been calculated, which suggest a tetragonal distortion for copper ion in the DZDBZ lattice. Extended our studies when dopant ion entre interstially how structure changed. FTIR and Powder XRD data confirms the structure of the lattice DZDBZ.

ACKNOWLEDGEMENTS

The author K.P thanks the University Grand Commission [33-316/2007(2007)] for financial assistance.
S.R thanks the DST-INSPIRE for financial assistance.
Supplementary Material: CCDC number: 787787 contain the supplementary crystallographic data for DZDBZ. These data can be obtained free of charge at ww.ccdc.cam.ac.uk/data.request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44−1223−336033; E–mail: deposit@ccdc.cam.ac.uk.

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