



Research Article

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Single Crystal EPR and Optical Studies of Vanadyl (II) Doped in Tetra aqua (1, 10-Phenanthroline-k2 N, N') Magnesium (II) Dinitrate

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Abstract

Single crystal EPR and optical investigation of vanadyl doped tetraaqua (1,10-phenanthroline-k² N,N')magnesium(II)dinitrate (abbreviated a TPMD) have been carried out at room temperature, using X-band frequencies. TPMD [Mg(C₁₂H₈N₂)(H₂O)₄-(NO₃)₂], belongs to monoclinic crystal class with space group C2/c having cell parameter a = 1.391, b = 1.048, c = 1.239 nm, $\alpha = \gamma = 90^\circ$, $\beta = 102.17^\circ$ and Z = 4 [1]. Magnesium atom coordinates with phenanthroline acting as a bidentate ligand through both N atoms. Four water molecules complete the environment around the metal atom with octahedral geometries. Single crystal rotations carried out in the three mutually orthogonal crystallographic planes namely ab, bc* and ac* indicate two chemical equivalent sites with different intensity. However, the second site could not followed due to it's weaker intensity and overlap with first site, during crystal rotations. The spin Hamiltonian parameters obtained for the site are: $g_{xx} = 1.977$ $g_{yy} = 1.971$ $g_{zz} = 1.939$; $A_{xx} = 6.00$, $A_{yy} = 6.44$, $A_{zz} = 16.86$ mT. These values agree well with reported data [2]. From the direction of cosines of principal g and A values, it has been confirmed that the impurity has entered the lattice interstitially. Admixture coefficients, Fermi contact (k) and dipolar interaction (P) have also been evaluated and the covalence of metal–ligand bond is deduced as 13%. Optical, IR and powder XRD techniques have been used to characterize the structure of the complex.

Keywords: Single crystal EPR, Octahedral geometries, Fermi contact, dipolar interaction, Hamiltonian parameters.

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1. Introduction

EPR studies on single crystals of paramagnetic ions generally provide detailed description on the nature of symmetry imposed by the ligands around the paramagnetic ions [1,2]. Vanadyl ion is the most stable diatomic ion known and has been extensively used as a probe to study the symmetry of crystalline electric field. EPR studies of VO(II) ion reveals interesting features about the structure, structural phase transitions of host lattice etc [3-6]. From the literature, it has been found that orientation of VO(II) ion can be classified into two types as VO(II) ion rotating

freely at room temperature and VO(II) ion as preferentially oriented. If the ligands present in the complex are water or sulphate ions, then VO(II) ion has fixed orientation while for other ligands it has random orientation. Extensive EPR studies have been reported on VO(II) ions in various host lattices [7-13]. In monoclinic crystalline symmetry, EPR analysis has shown that vanadyl has yielded two distinct sites whereas few others show two, three and four chemically distinct sites having two magnetically sites for each. Various forms of vanadium are proven to have insulinmimic effects [14]. The ability to substitute vanadyl ion for spectroscopically silent divalent cation, Such as Mg(II), Cd(II) and Zn(II) has lead to the increased use of vanadyl ion as spectroscopic probe of biological systems using techniques such as EPR[15]. EPR studies of VO(II) doped in arsanilic acid $[C_6H_4AsNO(H_2O)_2]$ indicate [16] that VO(II) ion is found to occupy interstitial position in the host lattice. Two vanadyl complexes have been identified corresponding to two vanadyl sites having distinct orientations. V=O bonds are found to be ionic in character.

When single crystal EPR studies of VO(II) ions doped in zinc lactate trihydrate $[Zn(CH_3CHOHCOO)_2 \cdot 3H_2O]$ point out that the vanadyl ions were found to occupy interstitial position in the lattice [17]. Wide-ranging EPR studies on VO(II) ion in an array of lattices have been reported [18,19]. Vanadium ions and complexes have been found to be very active to normalize the high blood glucose level in the patients with both type of DM (diabetes mellitus). Though ions exist in different valence states like divalent, trivalent and tetravalent [20,21], the vanadyl ion VO(II), is the most stable cation that is widely used as a paramagnetic probe for EPR studies. EPR studies on single crystals of VO(II) doped in phenanthroline complex of magnesium, $[Mg(C_{12}H_8N_2)(H_2O)_4](NO_3)_2$ have been carried out at room temperature. The detailed optical and EPR studies on this VO(II) impurity are presented in this chapter.

2. Materials and Methods

An aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ (60mg, 0.1mmol) and an ethanol solution of phenanthroline (40mg, 0.1mmol) were mixed and stirred for 30 minutes. To the resulting solution, about 1% vanadyl sulphate solution was added as paramagnetic impurity. Single crystals of tetraaqua(1,10-phenanthroline- k^2N,N')magnesium(II)dinitrate (abbreviated as TPMD) were grown by slow evaporation of the resulting solution at room temperature. Good, light green coloured, hexagonal shaped crystals were obtained in about 15 days. Single crystals of VO(II) doped in TPMD were studied at room temperature in the JEOL JES-TE 100 ESR spectrometer, having a modulation of 100 KHz and operating at x-band frequency. DPPH with a g value of 2.0036 is used for g-factor calculations. The spectra have been recorded for VO(II) doped in TPMD by rotating the crystal along the three mutually orthogonal axes, in steps of 10° rotation. EPR spectrum of powder sample is simulated using SimFonia program developed and supported by Bruker Company.

2.1. Crystal structure

Tetraaqua(1,10-phenanthroline)magnesium(II)dinitrate belongs to a group of compounds with general formula $[M(C_{12}H_8N_2)(H_2O)_4](NO_3)_2$ where M is a cation such as Co, Mg. TPMD is isostructural with tetraaqua(1,10-phenanthroline- k^2N,N')cobalt(II)dinitrate. The cobalt complex belongs to monoclinic crystal class with space group C_2/c . The unit cell dimensions for cobalt complex given are $a = 1.391$, $b = 1.048$, $c = 1.239$ nm and $\alpha = \beta = 90^\circ$, $\gamma = 102.165^\circ$ and $Z=4$. The structure consists of complex cations $[M(C_{12}H_8N_2)(H_2O)_4]^{2+}$ and nitrate anions which are linked together by hydrogen bonding. **Fig. 1** gives perspective view of complex cation of TPMD. The metal atom in complex cation, lying on a two fold rotation axis and is six coordinated by the two N atoms of a strong chelating phenanthroline ligand and four O atom of water molecules in an octahedral geometry. The two N atoms of phenanthroline and two water molecules are located (N_1, N_1^V, O_2, O_2^V) in equatorial plane, and the other two water molecules (O_1, O_1^V) occupy the axial positions. Two hydrogen bond motifs is to link the complex cations and nitrate anions into a three dimensional network. **Fig. 2** shows the perspective view of the three dimensional supramolecular TPMD crystal structure and hydrogen bonds within cations and anions. Each complex cation is hydrogen bonded ($O...H$) to six nitrate anions which in turn linked together eight cations. The structure is further stabilized by weak $\pi-\pi$ stacking interactions between two adjacent phenanthroline rings[22].

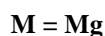
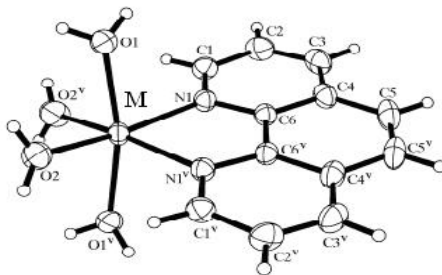


Figure 1. Perspective view of cation of TPMD complex

3. Results and Discussion

VO(II) ion has the electronic configuration $[Ar]3d^1$, which thereby leads to paramagnetism in VO(II). The 51V nucleus (99.8% abundant) has a nuclear spin $I=7/2$ and a large magnetic moment. Hence the EPR of VO(II) ions could consist of different orientations of VO(II) sites in a lattice. The EPR spectra are recorded for VO(II)/TPMD single crystal in the three mutually perpendicular planes ab , bc^* and ac^* at 10° regular intervals. Here axis a and axis b correspond to the crystallographic axis a and axis b , whereas axis c^* is perpendicular to the crystallographic ab plane. Crystals are grown with three different concentrations of dopant ion VO(II), with percentages namely 0.05, 0.10, 0.15% respectively. For crystal with dopant concentration of 0.05%, the resonance signals are very weak to follow, during crystal rotations. For the other two higher concentration crystals, it has been noticed that the intensities of the resonance lines increase as the vanadyl ion concentration increases. In the present investigation, only one site is observed even at the highest concentration studied. Single crystal EPR spectrum of VO(II)/TPMD recorded in ab plane, when the applied magnetic field (B) is parallel to axis a , is shown in **Fig. 3**. Reasonably sharp EPR spectra are observed, as the host is diamagnetic.

EPR spectrum consists of eight strong hyperfine lines, arising due to the interaction of a single unpaired electron ($S=1/2$) with 51V nucleus. These eight lines are not equal in intensity and spacing between them is not same. This immediately suggests the quadrupolar nature of the 51V nucleus. The isofrequency plot in ab plane is schematically given in **Fig. 4**. Single crystal of VO(II)/TPMD is rotated along axis a and EPR spectra at particular orientation is recorded at room temperature in the bc^* plane is given in **Fig. 5**. The isofrequency plot plotted for ac^* plane is given in **Fig. 6**. EPR spectra of VO(II)/TPMD recorded at room temperature for a orientation in the ac^* plane is shown in **Fig. 7**. One can also notice a few extra lines in **Fig. 7**, may be due to VO(II) in other sites. The weak lines could not be noticed at all orientations during crystal rotations due to overlap with strong lines. Hence, plotting the isofrequency plot in bc^* plane, only strong resonances are considered and is given in **Fig. 8**.

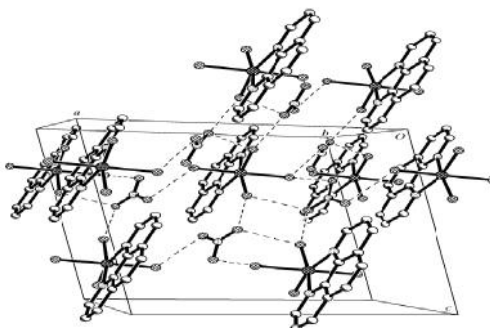


Figure 2. Perspective view of the three dimensional supramolecular TPMD crystal structure and hydrogen bonds within cations and anions.

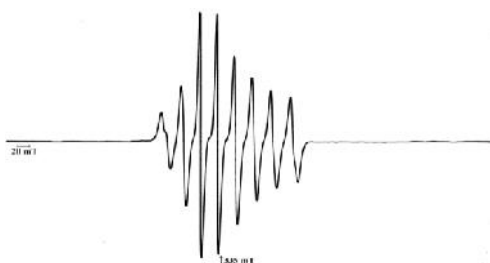


Figure 3. Single crystal EPR spectrum of VO(II)/TPMD in ab plane is recorded at room temperature, when the applied magnetic field (B) is parallel to axis a . Frequency = 9.04592 GHz.

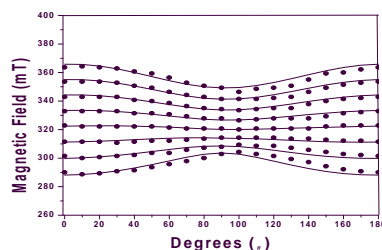


Figure 4. Angular variation of hyperfine lines for ab plane, when the crystal is rotated along axis c^* . The solid circles correspond to experimental values and solid lines are represented the theoretical values. Frequency = 9.04592 GHz.

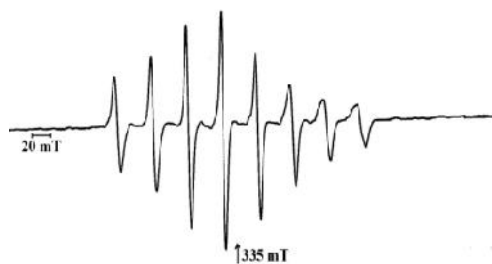


Figure 5. Single crystal EPR spectrum of VO(II)/TPMD in bc* plane is recorded at room temperature, when the applied magnetic field (B) is parallel to axis c*. Frequency = 9.04439 GHz

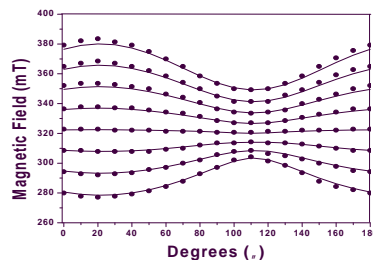


Figure 6. Angular variation of hyperfine lines for bc* plane, when crystal is rotated along axis a. The solid circles correspond to experimental values and solid lines are represented the theoretical values. Frequency = 9.04439 GHz.

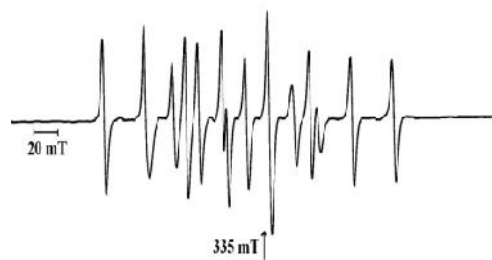


Figure 7. Room temperature single crystal EPR spectrum of VO(II)/TPMD in ac* plane, when the applied magnetic field (B) makes an angle 60° with the axis c*. Frequency = 9.04710 GHz.

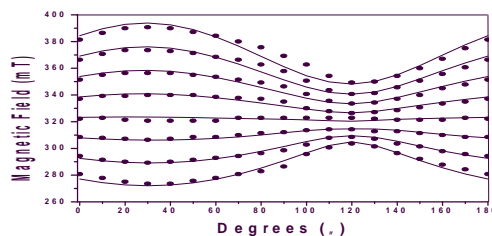


Figure 8. Angular variation of hyperfine lines for ac* plane, when crystal is rotated along axis b. The solid circles correspond to experimental values and solid lines are represented the theoretical values. Frequency = 9.04710 GHz

3.1. Spin-Hamiltonian parameters

EPR spectra of vanadyl complexes can be satisfactorily explained in terms of an unpaired electron ($S=1/2$) coupled with a vanadium nucleus ($I=7/2$). After identifying all the EPR transitions in the three planes, the spin-Hamiltonian parameters have been evaluated from the program EPR-NMR²³ using the spin-Hamiltonian,

$$H = [\beta_i(g_i \cdot B_i \cdot S_i) + S_i \cdot A_i \cdot I_i], \quad i = x, y \text{ and } z \quad (1)$$

where x , y and z are the principal axis of the g and A values and the symbols have their usual meaning. The principal values of the g and A , and their direction cosines are given in **Table 1**. Calculations have been reported by incorporating quadrupolar term in the Hamiltonian. However, no changes in g and A values were noticed. It is

clear from **Table 1** that the principal values of g and A are coincident. It is also confirmed from the isofrequency plots that the maxima and minima for g and A values occurred at the same angle. The g and A values given in **Table 1** represent the orthorhombic nature of the impurity. The direction cosines of various M-L bond directions in the lattice are calculated from X-ray data of the host lattice and are given in **Table 2**. These are necessary to locate the position of the dopant. The direction cosines of the principal values of g and A tensors, obtained from program EPR-NMR, do not match with any of the M-L bond directions, confirming that the VO(II) ion has entered the lattice in an interstitial position. Considering the structure of the host lattice, occupation of interstitial position is justified. Using these values and program EPR-NMR [23], the isofrequency plots have been simulated and are also given in **Fig. 4, 6 and 8**. In all these figures, the solid circles represent experimental points, whereas the continuous lines represent calculated points. A good agreement is noticed in all the three planes, confirming the accuracy of spin-Hamiltonian parameters.

In order to confirm single crystal data, powder EPR spectrum of the sample is recorded at room temperature and is given in **Fig. 9**. The calculated spin-Hamiltonian parameters for the powder sample are given in **Table 3** along with single crystal data. The powder values slightly differ from single crystal data. The orthorhombicity, noticed in single crystal data parameters, is generally not seen in powder spectrum, due to higher line widths in the latter. This is a common observation in all the VO(II) systems studied so far. Hence, in order to confirm the powder data, the EPR spectrum of the powder sample is simulated using the Bruker's SimFonia program with the data mentioned above and is shown in **Fig. 9**, along with the experimental spectrum. The agreement between the experimental powder spectra and the simulated powder spectra is relatively good.

Table 1. Spin-Hamiltonian parameters calculated for VO(II)/TPMD using program EPR-NMR [23]

g/A matrices			Eigen-values	Direction cosines		
				a	b	c*
g matrix			1.977 1.971 1.939	-0.546 -0.563 -0.619	0.748 -0.659 -0.060	-0.374 -0.496 0.782
1.960	-0.003	0.016				
	1.974	-0.000				
A matrix (mT)			6.44 6.01 16.86	-0.761 -0.294 -0.576	-0.347 0.937 -0.019	-0.546 -0.186 0.816
9.66	0.00	-5.08				
	6.40	2.43				
		13.26				

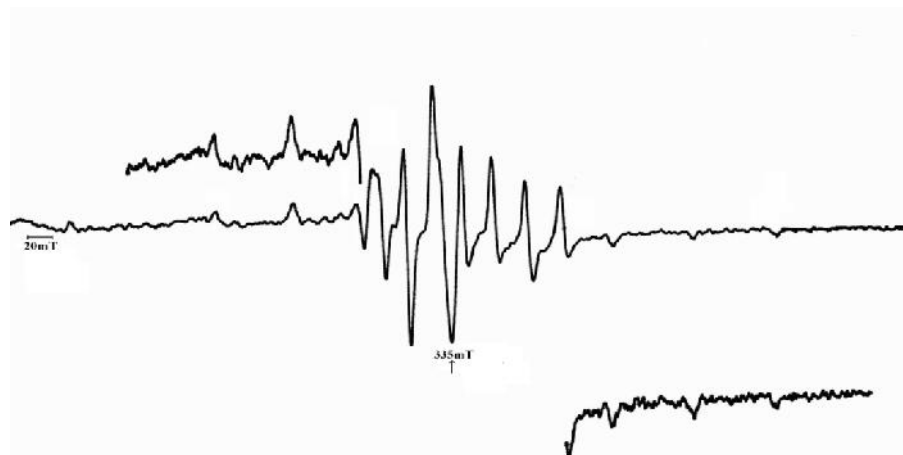


Figure 9. Powder EPR spectrum recorded at room temperature for VO(II)/TPMD. Top one is experimental and bottom one is simulated spectrum. Frequency = 9.34056 GHz

Table 2. Direction cosines of M-L bonds in TPMD lattice calculated from X-ray data[22]

Direction	A	B	c*
Mg-O ₁	-0.9878	-0.1098	0.1104
Mg-O ₂	0.0394	-0.6818	0.7305
Mg-N ₁	-0.2129	0.7785	-0.5904
Mg-N ₂	0.3849	0.3874	-0.3248

Table 3: Spin Hamiltonian parameters obtained at room temperature for VO(II)/TPMD from single crystal and powder data.

	g_{xx}	g_{yy}	g_{zz}	A_{xx} (mT)	A_{yy} (mT)	A_{zz} (mT)
Crystal	1.977	1.971	1.939	6.44	6.01	16.86
Powder	1.977	1.977	1.946	6.47	6.47	18.29

3.2. Admixture coefficients and other parameters

In order to get information regarding the mixing of ground state with excited state, the admixture coefficients (C_1 , C_2 , C_3), when the ground state d_{xy} mixes with $d_{x^2-y^2}$, d_{yz} and d_{xy} are calculated from the spin-Hamiltonian parameters, obtained from powder spectrum. These coefficients are calculated from the spin-Hamiltonian parameters by the equations [24].

$$g = 2(3C_1^2 - C_2^2 - 2C_3^2) \quad (2)$$

$$g = 4C_1(C_2 - C_3) \quad (3)$$

along with the normalization condition,

$$C_1^2 + C_2^2 + C_3^2 = 1.$$

The values are obtained by iterative procedure are given in **Table.4**, along with a few literature values. Using these coefficients and g/A parameters, two more parameters (A (Fermi contact term) and P (dipolar hyperfine coupling constant)) have also been calculated using the expressions

$$A = P\{(-4/7) - (3/7)(g - g_e)\} \quad (4)$$

$$A = P\{(2/7) - (11/14)(g - g_e)\} \quad (5)$$

Here P represents the dipole-dipole interaction of the electronic and nuclear moments ($P = g_e g_n \beta_e \beta_n \langle r^{-3} \rangle$), A is the Fermi contact parameter, which is related to the unpaired electron density at the vanadium nucleus and the other symbols have their usual meaning. The calculated values are given in **Table.5**, along with data from other systems. The standard value of P is 0.016 cm^{-1} . The percentage covalency calculated for the present system is 13%.

Table 4: Admixture coefficients of VO(II)/TPMD and similar host lattices

Lattice	C_1	C_2	C_3	References
TPMD	0.702	0.710	0.04	Present
DABMZ	0.702	0.711	0.04	[26]
MAPH	0.702	0.711	0.04	[27]
ZAPH	0.701	0.712	0.04	[28]
CAPH	0.702	0.711	0.04	[14]

CAPH = Cadmium ammonium phosphate hexahydrate

ZAPH = Zinc ammonium phosphate hexahydrate

MAPH = Magnesium ammonium phosphate hexahydrate

Table .5: Bonding parameters of VO(II)/TPMD and for similar host lattices

Lattice	$P(10^{-4} \text{ cm}^{-1})$	β^2	λ^2	λ^2	References
TPMD	-138	0.68	0.62	0.89	Present
ZLT	-133	0.86	0.85	0.13	[24]
CaF-SiF	-131	0.82	0.73	0.61	[29]
Kainite	-134	0.74	0.89	0.59	[2]

ZLT = Zinc lactate trihydrate

3.3. Calculation of molecular orbital bonding coefficients

The molecular orbital bonding (β^2 and λ^2), are calculated from the following formulae [25].

$$g = g_e - 8(\beta/E_1) \quad (6)$$

$$g = g_e - 2(\lambda^2/E_1) \quad (7)$$

Where the terms β^2 and λ^2 are bonding coefficients of $x^2 - y^2$ and (xz , yz) orbitals, which represent the in-plane π -bonding, respectively. λ is the spin-orbit coupling coefficient, which is assumed to be 170 cm^{-1} for VO(II) ion [25]. E_1 and E_2 are energy separation from the ground state ${}^2B_{2g}$ to the nearest excited states 2E_g and ${}^2B_{1g}$ respectively. g_e is the free electron g value ($g_e = 2.0023$). The values of molecular coefficients obtained in the present work are $\beta^2 = 0.62$ and $\lambda^2 = 0.81$ respectively. The parameters $(1 - \beta^2)$ and $(1 - \lambda^2)$ are the measure of the

covalency rates, the former gives an indication of the influence of π -bonding between vanadium atom and equatorial ligands while the latter indicates the influence of π -bonding the vanadyl oxygen. The calculated values of β^2 and β^2 indicate that both the in-plane π -bonding and the out-of-plane π -bonding is significantly ionic. The values of P , β^2 , β^2 and β^2 are calculated using the above expressions and are listed in **Table.5**, along with values for other host lattices. The parameter β^2 indicates extreme sensitivity to the deformations of the electron orbitals of the central vanadium ion. The large value of β^2 indicates a large contribution to the hyperfine constant by the unpaired s-electron and also probably a contribution from spin polarization. The calculated value of $P = -0.138\text{cm}^{-1}$ and $\beta^2 = 0.68$ in the present system.

3.4. Optical studies

The ground state term for VO(II) ion is 2D . In an octahedral symmetry, the d-electron occupies t_{2g} orbital and gives rise to $^2T_{2g}$ ground state. On excitation, the d-electron goes to e_g orbital and gives rise to 2E_g state. Thus only a single transition from $^2T_{2g}$ to 2E_g is expected for VO(II) ions in an octahedral symmetry. However, if the symmetry is lowered, the upper 2E_g splits into $^2B_{1g}$ and $^2A_{1g}$ and the lower level $^2T_{2g}$ splits into $^2B_{2g}$ and 2E_g , giving rise to more than one band. The optical absorption spectrum of VO(II) in TPMD is shown in **Fig.10**. It consists of four bands at $35,971\text{cm}^{-1}$, $24,038\text{cm}^{-1}$, $13,157\text{cm}^{-1}$ and $11,001\text{cm}^{-1}$. The strong band at $35,971\text{cm}^{-1}$ is assigned to charge transfer band, which usually occurs in the range $35,000\text{--}50,000\text{cm}^{-1}$. By comparison with the optical absorption spectra of other complexes containing VO(II), the other three bands are assigned to the transitions $^2B_{2g} \rightarrow ^2A_{1g}$, $^2B_{2g} \rightarrow ^2B_{1g}$ and $^2B_{2g} \rightarrow ^2E_g$ respectively [26]. This is shown in **Table.6**. The presence of three bands suggests that the distortion around the vanadyl ion can be attributed only to tetragonal but not to any other lower symmetry. The crystal field parameters for the vanadyl complex are calculated by the following relations [26].

$$^2B_{2g} \rightarrow ^2E_g = E1 = -3Ds + 5Dt \quad (8)$$

$$^2B_{2g} \rightarrow ^2B_{1g} = E2 = 10Dq \quad (9)$$

$$^2B_{2g} \rightarrow ^2A_{1g} = E3 = 10Dq - 4Ds - 5Dt \quad (10)$$

where Dq is the octahedral crystal field parameter, Ds and Dt are the tetragonal crystal field parameters. These evaluated parameters are:

$Dq = 1315.7\text{cm}^{-1}$; $Ds = -3126\text{cm}^{-1}$; $Dt = 324.6\text{cm}^{-1}$. These values are given in **Table.7**, along with other data from literature, for comparison.

Table 6. Optical absorption spectral data of VO(II)/TPMD at room temperature

Wave number (cm^{-1})	Wavelength (nm)	Assignment of Bands
35,971	283	CT Band
24,038	417	$^2B_{2g} \rightarrow ^2A_{1g}$
13,157	748	$^2B_{2g} \rightarrow ^2B_{1g}$
11,001	901	$^2B_{2g} \rightarrow ^2E_g$

Table 7. Crystal field parameters of VO(II)/TPMD and for similar host lattices

Lattice	$D_q \text{ cm}^{-1}$	$D_s \text{ cm}^{-1}$	$D_t \text{ cm}^{-1}$	References
TPMD	1315	-3126	324	Present work
$\text{MgTi}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1387	-2150	387	[13]
KRbB_4O_7	1666	-3219	507	[23]
$\text{Rb}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1612	-3919	390	[32]

These results indicate that the symmetry around the metal ion is nearly axially symmetric on optical time scale and slightly lowered further to orthorhombic on EPR time scale. Hence, one can conclude that the symmetry of the vanadyl ion is a distorted octahedron. The negative Ds value clearly indicates the nature of the distortion is elongation.

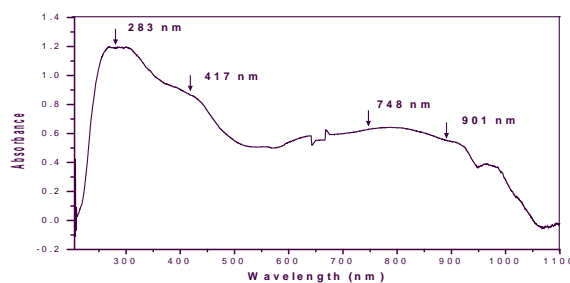


Figure 10. Optical absorption spectrum of VO(II)/TPMD at room temperature

3.5. IR studies

The infrared absorption spectrum is a unique characteristic of functional groups present in the molecule and is found to be a useful physical method for investigating the functional groups and to know the molecular structure [27]. In most of the vanadyl complexes, the V=O stretching band is observed between 1050 and 950 cm^{-1} . The IR spectrum of TPMD and VO(II)/TPMD is shown in **Fig.11**, assignment of the band positions are summarized in **Table.8**. From the band positions, it is inferred that that the grown crystal under investigation contains phenanthroline and water ligands. The presence of VO(II) ion is confirmed by the appearance of a band at 972 cm^{-1} .

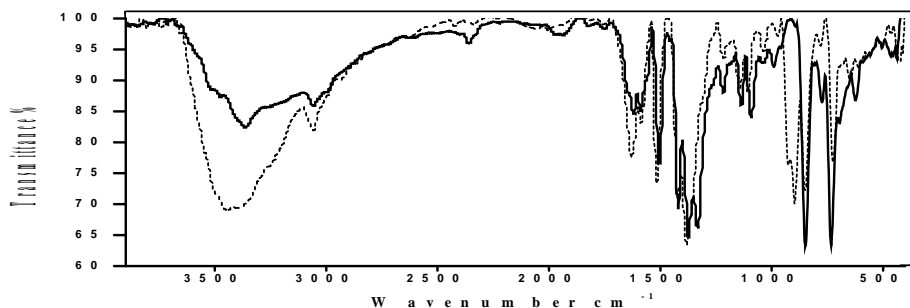


Figure 11. Powder FTIR spectra of TPMD (solid line) and VO(II) doped TPMD (Dashed line) at room temperature.

Table 8. Assignment of IR bands observed for VO(II) doped TPMD single crystal

Assignment	FTIR bands of VO(II) doped TPMD (cm^{-1})	FTIR bands of TPMD (cm^{-1})
O-H stretch	3445.2	3365.0
C-H stretch	3057.1	3059.3
C=N stretch	1629.9	1619.7
C=C stretch	1587.4	1589.2
C-N stretch	1380.8	1332.6
C-H (in plane bend)	1217.1	1217.4
C-H bend	1143.3	1136.4
V=O	972.5	-
Mg-N stretch	850.1	850.9
Mg-O stretch	780.6	774.1
C-C (out of plane bend)	724.8	732.9

3.6. Powder XRD

Powder XRD pattern of VO(II) doped TPMD at room temperature is shown in **Fig.12**. According to powder XRD measurements[28], VO(II) doped TPMD powder sample has identical lattice parameters as TPMD powder sample, as expected from the low impurity concentration. The lattice parameters are tabulated in **Table.9** with the single crystal XRD parameter of TPCD [22]. It is clear from the **table.9** that the parameters of TPMD and VO(II) doped TPMD matched with reported values of cobalt complex [22], confirming that the magnesium complex is isomorphic with cobalt complex and the low dopant concentration of VO(II) in TPMD does not alter the symmetry of host lattice.

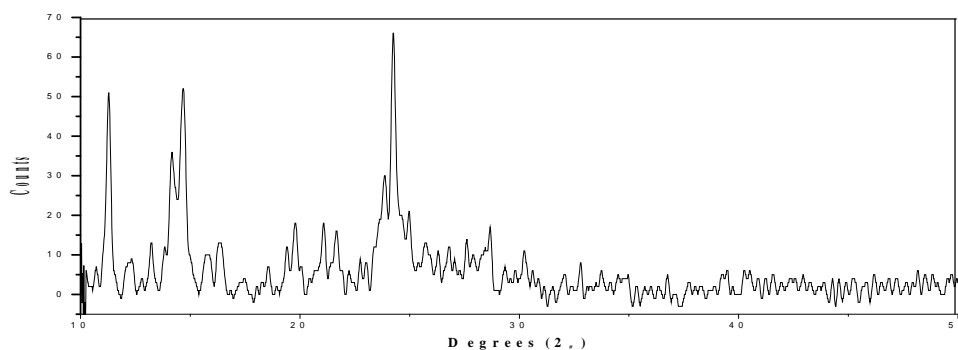


Figure 12. Powder XRD pattern of VO(II) doped TPMD at room temperature

Table 9. The calculated lattice parameters of TPMD and VO(II) doped TPMD from powder XRD, along with single crystal XRD of TPCD.

Lattice parameters (nm) of TPCD from single crystal XRD	Lattice parameters (nm) calculated from powder XRD	
	TPMD	VO(II) doped TPMD
a = 1.391	a = 1.451	a = 1.451
b = 1.048	b = 1.128	b = 1.128
c = 1.239	c = 1.245	c = 1.245

4. Conclusion

Single crystal vanadyl ion doped TPMD has been studied at room temperature using EPR technique indicates two sites present in the lattice is found to be independent of concentration of the impurity. We followed only one site because of the very low intensity of other sites. The spin Hamiltonian parameters have been evaluated which indicate that the impurity is rhombically distorted. It has been confirmed that the impurity has entered the lattice in substitutional position. The isofrequency plots and the powder EPR spectrum have been simulated, which authenticates evaluated spin Hamiltonian parameters. The optical absorption spectrum at room temperature shows three bands characteristic of vanadyl ions in distorted octahedral symmetry. Crystal field parameters are calculated using optical data. It indicates that the nature of the distortion is elongation. Admixture coefficients, Fermi contact term and dipolar interaction parameter have also been calculated. Mg – O, Mg – OH₂, -OH and O – C = O bonds are confirmed by FTIR. Powder XRD confirms the formation of the lattice TPMD.

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6. References

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