SPECTRAL INVESTIGATION OF VO(II) DOPED IN

\([\text{Zn(C}_{12}\text{H}_{8}\text{N}_{2})_2(\text{H}_2\text{O})_2] [\text{Zn(S}_2\text{O}_3)_2 (\text{C}_{12}\text{H}_{8}\text{N}_2)] \cdot \text{H}_2\text{O}\) SINGLE CRYSTAL: A CASE OF INTERSTITIAL AND SUBSTITUTIONAL SITES

6.1. Introduction

EPR spectroscopy, by virtue of it’s application to paramagnetic molecules, has become a major technique to gather information on the electronic structure and other related properties of the paramagnetic ion under study. The ligands around the metal ion dictate the properties of the paramagnetic guest. For example, oxoanions such as sulfates, sulfites and thiosulfates are highly versatile ligands and form stable, tight and compact three-dimensional structure complexes with most of the metal ions, due to their unique multidentate capacity [1, 2]. Regarding first-row transition metal ions, vanadium readily reacts to form a number of oxycations, the simplest being the vanadyl ion, VO(II). This vanadyl ion is the most stable cation among a few molecular paramagnetic transition metal ions that are used extensively as an impurity probe for EPR studies. The biological importance of vanadium is attributed to the fact that it is known to occur naturally in mushrooms and is as an essential cofactor in certain haloperoxidases and nitrogenases [3, 4]. Vanadium is responsible to be an essential trace element for humans as vanadate [5] and is known to affect phosphate metabolism. Various forms of vanadium have proven to have insulin mimetic effects [6]. Due to the possible different orientations of the V=O ion in metal complexes, the location of this ion in paramagnetic hosts may be either substitutional or interstitial or both. The ability of vanadyl ion to substitute for divalent
diamagnetic cations such as Mg(II), Ca(II) and Zn(II) has increased the use of this ion as a paramagnetic probe for biological systems using EPR, electron spin echo envelope modulation (ESEEM) and electron nuclear double resonance (ENDOR). The EPR of VO(II) ions, studied in a variety of lattices [7-16], fall into two categories, those in which the ion is free to rotate (at least at normal temperature) and those in which it is preferentially oriented. Since the vanadyl ion in different crystalline field environments is found to have interesting effects on the EPR spectra, single crystal and optical studies of VO(II) impurity in cis-diaquabis(1,10-phenanthroline-N,N')-zinc(II) (1,10-Phenanthroline-N,N') bis(thiosulfato-S)zincate(II) Monohydrate lattice have been undertaken.

6.2. Experimental

Single crystals of cis-diaquabis(1,10-phenanthroline-N,N')zinc(II) (1,10-Phenanthroline-N,N')bis(thiosulfato-S)zincate(II) Monohydrate (hereafter abbreviated as DPZSZM) doped with VO(II) were grown by slow evaporation method. The compound was prepared by mixing an alcoholic solution of phenanthroline with an aqueous solution of zinc acetate and sodium thiosulfate. To this a few drops of vanadyl sulphate solution were added as paramagnetic impurity. After a fortnight, well developed prismatic crystals were obtained.

EPR spectra were recorded on a JEOL JES TE100 ESR spectrometer operating at X-band frequencies, having a 100 kHz field modulation to obtain a first derivative spectrum. DPPH with a g value of 2.0036 was used for g-factor calculations. Crystals of 2 mm thickness were selected for optical absorption studies and the spectra were
recorded in UV-VIS region on Varian Cary 5000 UV-visible NIR spectrophotometer at room temperature (RT) in the range of 200–1200 nm. For IR studies, a small sample of the VO(II)/DPZSZM was taken and ground to a fine powder along with KBr to form a pellet. The infrared spectrum was recorded on BOMEM MB 104 FT-IR spectrometer in the range of 4000–500 cm\(^{-1}\).

6.3. **Crystal Structure**

\[[\text{Zn(C}_{12}\text{H}_8\text{N}_2\text{)}_2(\text{H}_2\text{O})_2][\text{Zn(S}_2\text{O}_3\text{)}_2(\text{C}_{12}\text{H}_8\text{N}_2\text{)}\text{]}\text{H}_2\text{O}] \text{ (DPZSZM)}\] belongs to the triclinic crystal class, having space group \(P^-1\) with unit cell parameters \(a = 1.0545, b = 1.2924, c = 1.4856\) nm, \(\alpha = 90.60^\circ\), \(\beta = 100.06^\circ\), \(\gamma = 99.47^\circ\) and contains two molecules per unit cell [17]. The structure consists of cationic \([\text{Zn(C}_{12}\text{H}_8\text{N}_2\text{)}_2(\text{H}_2\text{O})_2]\)^{2+} and anionic \([\text{Zn(S}_2\text{O}_3\text{)}_2(\text{C}_{12}\text{H}_8\text{N}_2\text{)}\text{]}\)^{2-} moieties. Fig. 6.1 shows the structure of moieties and the crystal packing. \([\text{Zn(C}_{12}\text{H}_8\text{N}_2\text{)}_2(\text{H}_2\text{O})_2]\)^{2+} cation is in a distorted octahedral coordination with phenanthroline acting as a bidentate ligand through both N atoms. The fifth and sixth coordination around the metal ion are occupied by two water molecules. However, the coordination geometry of metal in \([\text{Zn(S}_2\text{O}_3\text{)}_2(\text{C}_{12}\text{H}_8\text{N}_2\text{)}\text{]}\)^{2-} anion is distorted tetrahedral with both thiosulfate groups bonded to the Zn atom through sulfur and phenanthroline occupying the other two coordination sites. The three independent phenanthroline molecules in the cell have distances and angles that are in good agreement with the values reported for the free base [18] and also in many other zinc complexes [19]. Angular variations for single crystals of DPZSZM are made at room temperature by rotating the crystals along the three mutually orthogonal axes \(a^\ast\), \(b\) and \(c^\ast\). Axis \(c^\ast\) lies in the crystal bc plane making an angle of 90° to axis \(b\) and axis \(a^\ast\) is orthogonal to
both axes b and c*, so that when a* is perpendicular to B, the magnetic field traverses the
crystal bc plane (which is also the bc* plane).

6.4. Results and discussion

From the batch of crystals, one with well defined faces was selected for single
crystal rotations along the three axes. The EPR spectrum of VO(II) doped DPZSZM
crystals, recorded when the applied magnetic field (B) is making an angle of 100°
degrees with axis c* (Plane 1) is shown in Fig. 6.2. Since the nuclear spin of $^{51}\text{V}$ is 7/2,
an eight line pattern is expected for a vanadyl impurity, when the applied magnetic field
is parallel to any crystallographic axis. Fig. 6.2 consists of two sets of eight resonance
lines, indicated by 1-8 (Site 1) and a less intense another set of eight lines, indicated by
a-h (Site 2). The intensity ratio of these two sites is approximately 12:8. This spectrum
is due to the interaction of a single electron (S=1/2) with $^{51}\text{V}$ nucleus (I=7/2). When the
crystal is rotated in this plane, the site with higher intensity splits into two, whereas the
other set does not. This is shown in Fig.6.3. Here, 1-8 and 1’-8’ belong to Site 1 and a-h
belongs to Site 2. One can also notice a few extra weak lines in Fig. 6.3, may be due to
VO(II) in other sites. However, these lines are too low in intensity to follow through
crystal rotations. Hence only the two dominant sites are only considered for analysis.
The angular variation plot in this Plane 1 is drawn and shown in Fig 6.4. In this plot,
solid and open circles correspond to a*c* plane of Site 1 and star signs denotes bc* plane
of Site 2. Crystal was mounted along another axis and a typical spectrum in this Plane 2
is shown in Fig. 6.5. As mentioned earlier, here also, one can notice two sites and the
behavior of these sites is similar to the one mentioned in Plane 1. Isofrequency plot in
this plane is given in Fig. 6.6. Fig. 6.7 and Fig. 6.8 correspond to spectrum and angular variation of hyperfine lines in Plane 3. It is generally expected for an axially symmetric impurity, the angular variation of resonance lines in one plane are invariant (XY plane), where as the angular variation in the other two planes (XZ and YZ) will be same. Any deviation from axial symmetry makes XY plane resonances variant and resonances in XZ/YZ planes are not equal. With this background, the resonances in three planes have been classified as follows for obtaining spin Hamiltonian parameters. In Fig. 6.4, the angular variation of resonances for Site 1 belong to a*c* plane, where the resonances of Site 2 belong to bc* plane. In Fig. 6.6, the angular variation of resonances for Site 1 belong to bc* plane, where the resonances of Site 2 belong to a*b plane. In Fig. 6.8, the angular variation of resonances for Site 1 belong to a*b plane, where the resonances of Site 2 belong to a*c* plane. Here, we want to mention that the unit cell contains two molecules per unit cell.

6.4.1. Spin Hamiltonian Parameters

All the transitions have been identified and the spin Hamiltonian parameters have been evaluated from the program EPR–NMR [20] and the isofrequency plots, using the spin Hamiltonian

$$\mathcal{H}_S = \beta (g_x B_x S_x + g_y B_y S_y + g_z B_z S_z) + A_{xx} S_x I_x + A_{yy} S_y I_y + A_{zz} S_z I_z$$

(1)

where the symbols have their usual meaning; the quadrupole and nuclear Zeeman interaction terms are ignored. The spin-Hamiltonian parameters thus obtained are given in Table 6.1. Using the parameters given in Table 6.1, isofrequency plots in the three planes are simulated and are found to agree well with the experimental ones. The resultant isofrequency plots obtained for all the three planes, containing the experimental
and theoretical values are shown in Fig. 6.3, 6.5 and 6.7. This further confirms the accuracy of the evaluated spin Hamiltonian parameters. The following observations can be made from Table 6.1. The deviation from axial symmetry is reflected more in $A$ values and that too in Site 1. The direction cosines of $g$ and $A$ are coincident, as also evidenced from isofrequency plots (maxima and minima occurred at the same angle for $g$ and $A$ variation). Hence, in order to identify the location of the vanadyl impurity, the direction cosines of various Zn-Ligand direction cosines have been calculated from X-ray data and are given in Table 6.2. As one site is showing splitting of resonances during crystal rotation, it should have occupied a substitutional position; whereas the other site might have entered interstitially. However the direction cosines of $\text{Zn}_2-O_1W$ matched with Site 1 directions. This immediately suggests that one vanadyl ion (Site 1) the impurities might have entered the lattice substitutionally. It is clearly shown in Fig. 6.9. The direction cosine of the principal value of $g$ tensor of Site 1 is approximately along $\text{Zn}_2-O_1W$ direction, the deviation being around 23°, respectively. The direction cosine of Site 2 does not match with the Zn-Ligand direction cosines. So the second sight of the vanadyl entered the lattice interstitially. Due to different coordination sites available in the complex, the impurity has chosen interstitial substitution due to the rigid nature of ligands, surrounding the metal ions. Due to the complex nature of structure, we could not locate the exact location of the interstitial position.

6.4.2. Polycrystalline spectra

EPR spectrum of the polycrystalline sample is recorded at room temperature and is shown in Fig. 6.10. The spectrum consists of only one site, even though two sites are noticed in single crystal analysis. As the two sites observed in single crystal analysis are
magnetically inequivalent, but chemically equivalent, only one set of hyperfine lines are observed. The principal g and A parameters have been calculated from the polycrystalline spectrum and are given below.

\[ g_\parallel = 1.9315; g_\perp = 1.9861; A_\parallel = 20.17 \text{ mT}; A_\perp = 7.56 \text{ mT} \]

Due to the closeness of g and A values for x and y components (corresponding to the parallel directions), these are not resolved in the powder spectrum, which is a common observation for VO(II) impurities. These parameters are coinciding with the principal values obtained from the single crystal EPR Spectra for both the sites. Since the polycrystalline EPR spectrum has shown that all the vanadyl complexes in the host under consideration are essentially identical in nature, the powder EPR data are used for the calculation of Admixture coefficients. The powder EPR spectrum at RT is simulated using SimFonia program. The simulated spectrum is also given in Fig. 6.10.

6.4.3. Admixture coefficients

The admixture coefficients which provide information about the mixing of ground state with the excited state are also calculated from the spin-Hamiltonian parameters. If \( C_1, C_2 \) and \( C_3 \) are the admixture coefficients, where the ground state \( d_{xy} \) mixes with \( d_{x^2-y^2} \); \( d_{yz} \) and \( d_{xy} \); these are related to the spin-Hamiltonian parameters by the relations

\[ g_\parallel = 2(3C_1^2-C_2^2-2C_3^2) \]  \hspace{1cm} (2)
\[ g_\perp = 4C_1 (C_2-C_3) \]  \hspace{1cm} (3)

These equations along with the normalization condition \( (C_1^2+C_2^2+C_3^2 = 1) \) are solved iteratively to obtain the admixture coefficients. The obtained values are \( C_1 = 0.7013 \), \( C_2 = 0.7117 \) and \( C_3 = 0.0404 \). The dipolar coupling constant (P) and Fermi contact coupling parameter (\( \kappa \)) are evaluated using the formula

96
where \( g_e \) is 2.0023. The standard value of P is \( 160 \times 10^{-4} \) cm\(^{-1}\). The obtained values are : \( \kappa = 0.836 \) cm\(^{-1}\), \( P = -136 \times 10^{-4} \) cm\(^{-1}\). The values of P and \( \kappa \) are listed along with other lattices for comparisons in Table 6.3.

6.5. Optical spectrum

VO(II) ion belongs to \( d^1 \) configuration and will have a ground state of \( ^2D \). In the presence of pure octahedral crystal field, the \( ^2D \) state splits into \( ^2T_{2g} \) and \( ^2E_g \), while an octahedral field with tetragonal distortion further splits the \( ^2T_{2g} \) level into \( ^2E_g \) and \( ^2B_{2g} \) and \( ^2E_g \) level splits into \( ^2A_{1g} \) and \( ^2B_{1g} \). Among these, \( ^2B_{2g} \) will be the ground state. Thus for vanadyl ions, we can expect three bands corresponding to the transitions \( ^2B_{2g} \rightarrow ^2E_g \), \( ^2B_{2g} \rightarrow ^2B_{1g} \) and \( ^2B_{2g} \rightarrow ^2A_{1g} \). The optical absorption spectrum (Fig. 6.11) exhibits two bands corresponding to d-d transitions, characteristic of VO(II) ions in tetragonal symmetry. The two bands have been assigned to the transitions \( ^2B_{2g} \rightarrow ^2B_{1g} \) and \( ^2B_{2g} \rightarrow ^2E_g \) in the decreasing order of energy respectively.

6.5.1 Calculation of the molecular orbital coefficients

The molecular orbital coefficients \( \beta_1^2 \) and \( \epsilon^2 \) are estimated from the following expressions [21]

\[
\beta_1^2 = \frac{(g_e - g_{||}) \Delta_{||}}{8 \lambda d} \quad (6)
\]

\[
\epsilon^2 = \frac{(g_e - g_{\perp}) \Delta_{\perp}}{2 \lambda} \quad (7)
\]

where \( \beta_1^2 \) and \( \epsilon^2 \) are bonding coefficients of \( |x^2-y^2> \) and \( |xz, yz> \) orbital respectively. \( \lambda \) is the spin orbit coupling constant which is assumed to be equal to 170 cm\(^{-1}\) for VO(II) ion.
\[ \Delta_{||} \text{ and } \Delta_{\perp} \text{ are the energy separations between the ground state (}^2B_{2g}\text{) and the two next higher states (}^2E_g \text{ and } ^2B_{1g}\text{) respectively. Using the EPR and optical data, Eqs (6) and (7) can be solved to get } \beta_1^2 \text{ and } \varepsilon_2^2. \text{ If } \beta_1^2 = 1, \text{ the bond would be completely ionic and if } \beta_1^2 = 0.5, \text{ the bond will be completely covalent. In the present investigation } \beta_1^2 = 0.909 \text{ and } \varepsilon_2^2 = 0.596. \text{ The values show that the covalency rate of the } \sigma \text{ bonding is 90 \% and that of the } \pi \text{ bonding is 40 \%. The parameters } (1 - \beta_1^2) \text{ and } (1 - \varepsilon_2^2) \text{ are the measures of covalency rates. First term gives an indication of the influence of } \sigma \text{ bonding between vanadium atom and equatorial ligands, where as the second indicates the influence of } \pi \text{ bonding between the vanadium ion and the vanadyl oxygen. It is known that a high value of } 1 - \beta_1^2 \text{ indicates strong covalent in-plane } \sigma \text{ bonding, while } 1 - \varepsilon_2^2 \text{ suggests moderate covalent out of plane } \pi \text{ bonding. Also, } \varepsilon_2^2 \text{ is less than } \beta_1^2 \text{ indicating that the in-plane } \sigma \text{ bonding is more ionic and out-of plane } \pi \text{ bonding is moderately covalent in nature [23, 24]. In the present work, } \varepsilon_2^2 \text{ is less than } \beta_1^2 \text{ indicating that the in-plane } \sigma \text{ bonding is significantly ionic and out-of plane } \pi \text{ bonding is moderately covalent. The calculated values of } \beta_1^2 \text{ and } \varepsilon_2^2 \text{ are listed with similar lattices for comparison in Table 6.3.}

### 6.6. IR spectrum

The strong band position at 991 cm\(^{-1}\) corresponds to stretching vibration of V=O (Fig. 6.12). IR spectra of zinc complexes correspond to stretching bands at 1392 cm\(^{-1}\), 1355 cm\(^{-1}\) and 1191 cm\(^{-1}\). The bending mode of SO\(_4^{2-}\) occurs at 617 cm\(^{-1}\). The ligand shows bands at 3132, 3259 cm\(^{-1}\) which may be attributed to –NH vibrations [28] and the band at 1622 cm\(^{-1}\) is assigned to (>C=N) stretching [29]. The broad composite bands extending from 3200–3600 cm\(^{-1}\) are attributed to hydroxyl or water groups. The
absorption bond at 3450 cm$^{-1}$ is attributed to O–H stretching vibration. However, the bands arising from Zn–O and stretching vibrations are usually observed around 418 cm$^{-1}$ [27].

6.7. Conclusion

The present systematic study indicates that two vanadyl ions entered the lattice, while one is substitutional and the other is interstitial into the DPZSZM lattice, when doped with vanadyl sulphate. The spin Hamiltonian parameter values obtained from the single crystal and powder spectrum match with one another, confirming the accuracy of the single crystal EPR analysis. By correlating EPR and optical data, the molecular orbital coefficients have been evaluated. From the values of $\varepsilon_2^2$ (0.7-0.9) the out of plane $\pi$ bonding is significantly ionic and the values of $\beta_1^2$ (0.5) show that the in-plane $\sigma$ bonding is moderately covalent. From the values of $\beta^2$ and $\varepsilon^2$ it can be confirmed that the in-plane $\sigma$ bonding is significantly ionic, while the out of plane $\pi$ bonding is moderately covalent. The infrared bands confirm the lattice structure.
References


