EPR and Optical Absorption Studies of VO^{2+} Doped *Tri*sodium Citrate Dihydrate Single Crystals

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The electron paramagnetic resonance of VO^{2+} doped *tri*sodium citrate dihydrate ($Na_3C_6H_5O_7\cdot 2H_2O$) single crystals and powder has been examined at room temperature. The angular variation of the EPR spectra has shown that two different VO^{2+} complexes are located in different chemical environments, each environment containing two magnetically inequivalent VO^{2+} sites in distinct orientations occupying substitutional positions in the lattice and showing a very large angular dependence. The crystalline field around the VO^{2+} ion is nearly axial. The optical absorption spectrum shows three bands, centered at 24631, 16892, and 12195 cm^{-1}. The spin Hamiltonian parameters and the molecular orbital coefficients are calculated from the EPR and optical data, and result are discussed.

Key words: EPR; *Tri*sodium Citrate; Absorption the Spectrum; Vanadyl Ion.

1. Introduction

VO^{2+} is one of the most stable cations among a few molecular paramagnetic transition metal ions, and it is extensively used as impurity probe for electron paramagnetic resonance (EPR) studies, which is sensitive to the crystal environment. VO^{2+} complexes have been studied by several authors in recent years [1 – 10]. When VO^{2+} is doped in a diamagnetic crystal as an impurity, it forms complexes having various ligands filling its environment. Some of these environments are clearly resolved. The behaviour of the unpaired electron in a VO^{2+} complex is dominated by the strong V=O bond. It is also interesting and productive to study the local symmetry and the bonding of the vanadyl complex by correlating EPR and optical absorption data.

*Tri*sodium citrate dihydrate is a tribasic salt of citric acid. It is widely used in foods, beverages and various technical applications, mainly as buffering, sequestering or emulsifying agent. It is also important in biological and medical applications [11 – 12]. EPR studies of VO^{2+} in *tri*sodium citrate pentahydrate, *tri*potassium citrate monohydrate and *tri*ammonium citrate monohydrate have been reported [13 – 15]. In the present work we have undertaken the resolution and identification of VO^{2+} complex spectra in trisodium citrate dihydrate single crystal and powder. The single crystal EPR spectrum contains a large number of lines which make the resolution rather difficult. So a numerical technique is used to evaluate the spectra given in some previous papers [16 – 21].

2. Experimental

*Tri*sodium citrate dihydrate [$Na_3C_6H_5O_7\cdot 2H_2O$; TSCD hereafter] was obtained from Merck. It was recrystallized from stirred saturated aqueous solutions containing 0.3% $VOSO_4\cdot 3H_2O$. Well developed single crystals of suitable size were selected after about one week. TSCD crystallizes in monoclinic symmetry. The unit cell dimensions are $a = 15.70$ Å, $b = 12.50$ Å, $c = 11.28$ and $\beta = 103.58^\circ$. There are eight molecules in a unit cell [22].

The EPR spectra were recorded with a Varian E-109 C model X-band EPR spectrometer using 2 mW microwave power and 100 kHz magnetic field modulation. The single crystal was glued on a quartz tube and rotated in three mutually perpendicular crystalline planes (a^*c, a^*b, bc, respectively). The spectra were recorded with 10° steps in each plane. The g factors were corrected by comparing with a diphenylpicrylhydrazyl sample ($g = 2.0036$). The optical absorption spectra of the TSCD single crystals were recorded at

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Table 1. Principal values of **g** and hyperfine (**A**) tensors for paramagnetic vanadyl complexes in TSCD single crystals at room temperature ($\Delta g = \pm 0.005$ and A and P are in units of 10^{-4} cm^{-1}).

Complex no	site	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	β_1^2	β_2^2	γ^2	κ	P	$\Delta g_\parallel/\Delta_\perp$
I	1	1.935	1.998	181.3	59.1	0.90	0.93	0.17	0.67	142	15.6
	2	1.935	1.997	180.8	60.2	0.90	0.93	0.20	0.69	140	12.6
II	1	1.937	2.000	181.7	58.0	0.87	0.93	0.09	0.67	144	28.3
	2	1.938	1.999	181.4	60.7	0.86	0.93	0.13	0.69	140	19.4
Powder		1.938	1.998	183.7	64.4	0.86	0.93	0.16	0.72	138	14.9

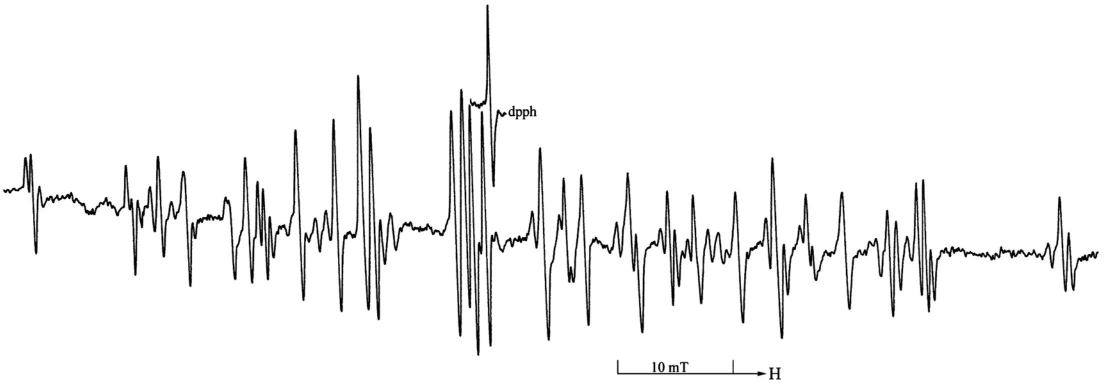

Fig. 1. EPR spectrum of VO^{2+} doped TSCD single crystal. The magnetic field is in the *bc* plane making 140° with the *b* axis.

room temperature on a CINTRA 20 UV-VIS spectrometer with diffuse reflectance accessory working between 300 and 900 nm.

3. Results and Discussion

The EPR spectra of VO^{2+} doped TSCD single crystals yield a large number of lines originating from different orientations of VO^{2+} sites in the lattice. The number, position and spacings of the lines are highly dependent on the orientations. The lines appearing at one orientation disappear almost completely at some other orientation, so it is too difficult to trace all of the lines in all orientations. We therefore used a simple technique to resolve and identify the lines as given in previous papers [16, 19]. The EPR spectra, recorded when the magnetic field makes 140° from the *b* axis in the bc plane is shown in Figure 1. The spectrum consists of four sets of octets, as seen in the figure. The octets in each set are obviously due to the interaction of a single unpaired electron with the vanadium nucleus ($I = 7/2$).

The g^2 values of all detected single lines are ploted against the rotation angle in mutually three perpendicular planes, as shown in Figure 2. The g^2 variation of a line with respect to the rotation angle in each plane must fit to the expression

$$g^2(\theta) = g_{ii}^2 \cos^2\theta_{ii} + g_{jj}^2 \sin^2\theta_{jj} + 2g_{ij}^2 \cos\theta_i \sin\theta_j, \quad (1)$$

where $i, j, k = x, y, z$ are cyclical coordinates and θ is the rotation angle. g_{ii}^2, g_{jj}^2 and g_{ij}^2 are the **g** tensor elements which will be found after least squares fitting [18]. Four sets of octets are clearly resolved, as shown Figure 2. When the magnetic field is in the a^*c plane, however, they merge into two octets.

The spectrum can be described in terms of a spin Hamiltonian of the form

$$\begin{aligned} H = {} & \beta[g_{xx}H_xS_x + g_{yy}H_yS_y + g_{zz}H_zS_z] \\ & + A_{xx}I_xS_x + A_{yy}I_yS_y + A_{zz}I_zS_z. \end{aligned} \quad (2)$$

The g and A values are calculated by means of an iterative numerical technique [23]. The results are given in Table 1. The behavior of the unpaired electron in vanadyl complexes is determined by a strong V=O bond. As a result, both g and A of all complexes are found to be nearly axially symmetric, as usual for most of the VO^{2+} complexes reported in the cited papers [13 – 15].

At first the spectra seem to be incompatible with the monoclinic symmetry, for in the a^*c plane the hyperfine lines do not merge into a single set. Referring to the spectral behavior, the complexes can be collected into two groups, each having two complex sites.

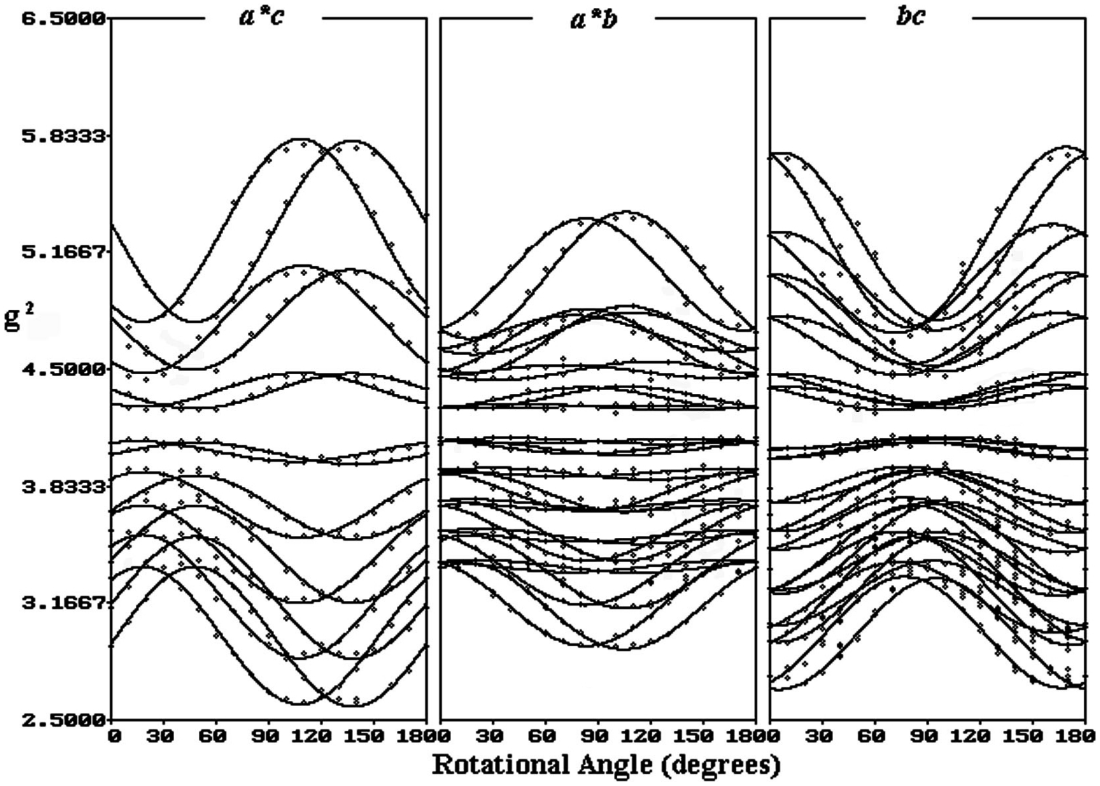

Fig. 2. Variations of g^2 values of all lines in three mutually perpendicular planes of VO^{2+} doped TSCD single crystal.

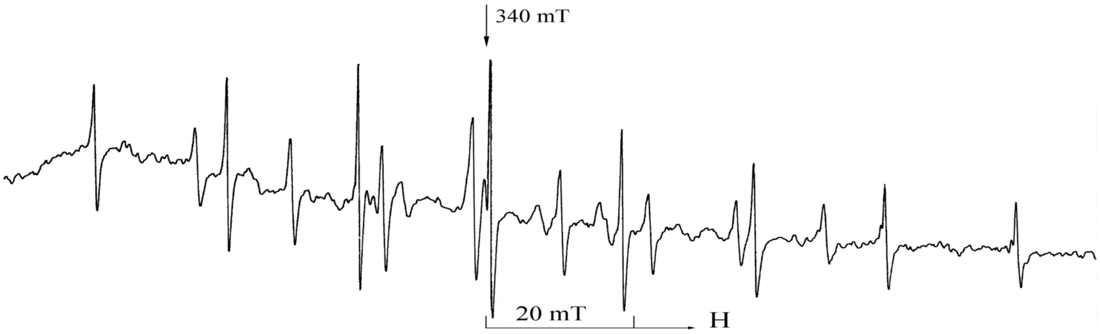

Fig. 3. EPR spectrum of VO^{2+} doped TSCD single crystal. The magnetic field is in the a^*c plane making 80° with the c axis.

In other words, there are two different VO^{2+} complex groups located in different chemical environments, and each environment contains two magnetically distinct sites. Moreover, in the a^*c plane, when the magnetic field makes 140° with the c axis, triplet super hyperfine splittings are clearly resolved, Figure 1. These splittings arise from equivalent hydrogen atoms of one of the H_2O molecules in the ligand position [8]. The splittings are about 1 mT. The same result was observed in some VO^{2+} complexes [17, 18].

The line intensity ratio of two different complexes located in different positions are about 2 to 1, which shows the proportion of the populations of the different complexes, Figure 3.

The spectra show that the vanadium ion of the $V^{4+} = O^{2-}$ group replaces the Na^+ in the host lattice; since V^{4+} is more active and smaller (the atomic radii are 0.98 Å for Na^+ and 0.61 Å for V^{4+}). VO^{2+} coordinates with one H_2O molecule in the axial position of the octahedron, and two citrate groups in the equa-

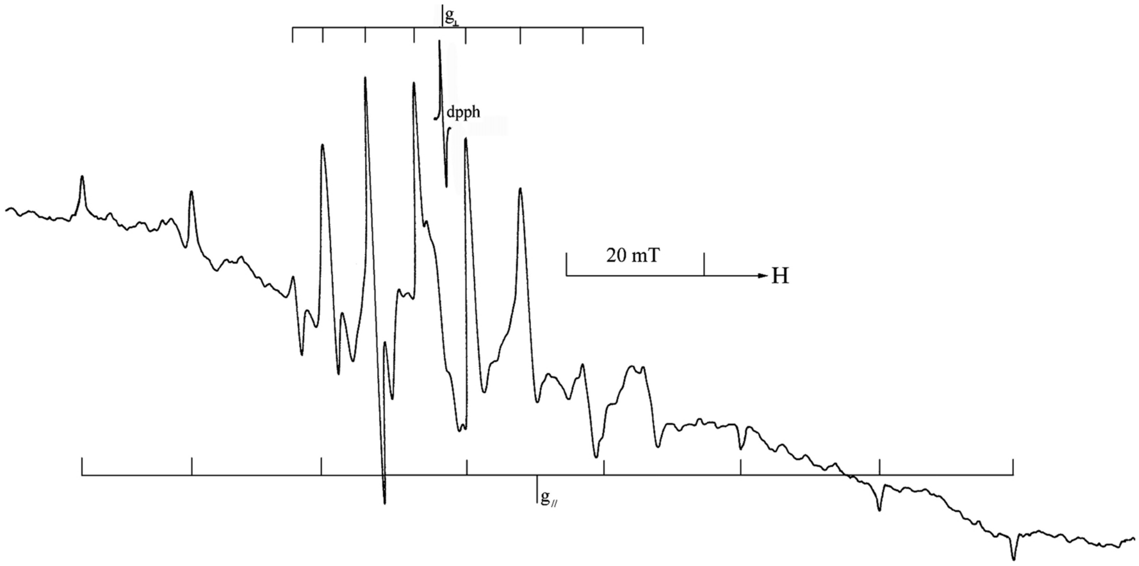

Fig. 4. Powder spectrum of VO^{2+} doped TSCD.

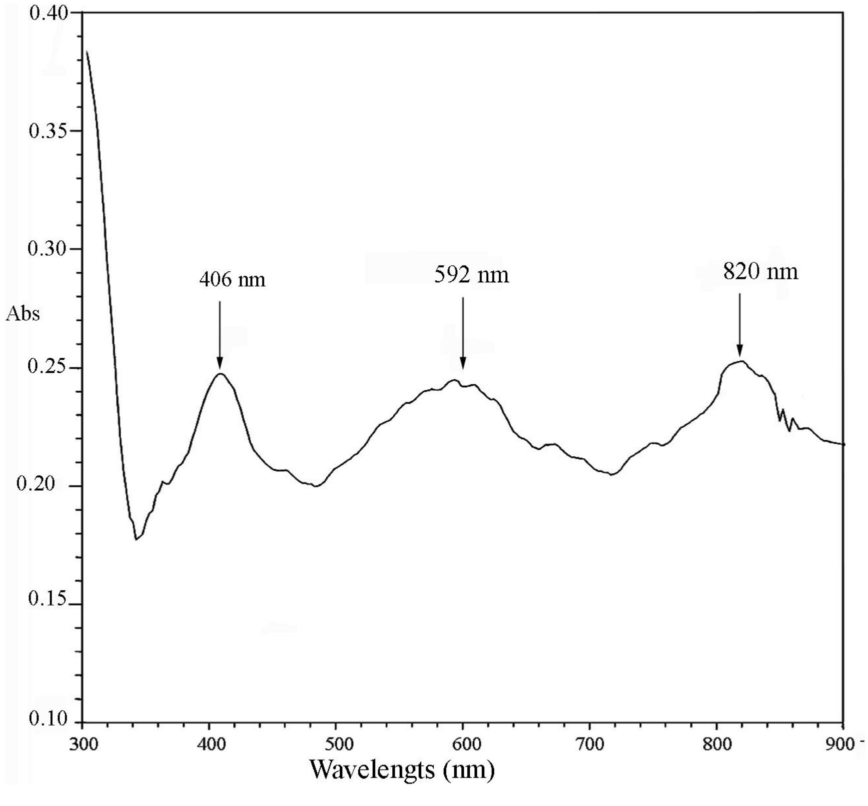

Fig. 5. Optical absorption spectrum of VO^{2+} doped in TSCD single crystal.

torial plane bidentally [22]. The charge compensation is fulfilled by a proton vacancy of the citrate group. VO^{2+} sites occupy substitutional positions in the lattice with fixed orientations and show very high angular dependence. An octahedral complex with a tetragonal compression would give $g_{\parallel} < g_{\perp} < g_e$. Referring to Table 1 we obtained the tetragonality measure $(g_e - g_{\parallel})/(g_e - g_{\perp})$ to be high, showing that the octahedron is tetragonally distorted [24].

The powder spectrum of TSCD recorded at room temperature is shown in Figure 4. The Parallel and perpendicular components of the VO^{2+} complex are clearly resolved, and the parameters are found to be $g_{\perp} = 1.998$, $g_{\parallel} = 1.938$, $A_{\perp} = 6.90$ mT, and $A_{\parallel} = 19.6$ mT. The VO^{2+} ion is known to form an octahedral oxygen complex, and the V=O direction will be the predominant axial direction. Powder and single crystal data give the same g and A values, as seen in Table 1.

Figure 5 shows the optical absorption spectrum of VO^{2+} in TSCD single crystals at room temperature. In an octahedral crystal field, the d^1 electron occupies the lowest-lying orbital $^2T_{2g}$, the next excited state being $^2E_{2g}$. The optical absorption spectrum consists of three absorption bands centred at 12195, 16892, and 24631 cm^{-1}. These three bands are typical for VO^{2+} and can be assigned to $\Delta_{\perp} = {}^2B_{2g} \rightarrow E_{2g}$, $\Delta_{\parallel} = {}^2B_{2g} \rightarrow {}^2B_{1g}$, and $\Delta = {}^2B_{2g} \rightarrow {}^2A_{1g}$ transitions, respectively. The parallel components of the **g** and **A** tensors are not collinear due to the distortion of octahedrons in the environments where they are settled. The distortion takes place along the V=O directions, and the degeneracy of the ground state d_{xy} of the vanadium atom in $3d^1$ configuration splits into $d_{x^2-y^2}$, d_{xz} and d_{yz} states [25–27]. The values of $g_{\parallel}$ and $g_{\perp}$ are related to the bonding parameters by the equations

$$g_{\parallel} = g_e\left(1 - \frac{4\lambda\beta_1{}^2\beta_2^2}{\Delta_{\parallel}}\right), \quad (3)$$

$$g_{\perp} = g_e\left(1 - \frac{\gamma^2\beta_2^2}{\Delta_{\perp}}\right), \quad (4)$$

where $g_e (= 2.0023)$ is the free electron g value and λ the spin orbit coupling constant of the VO^{2+} ion. The value of $\lambda = 170\ cm^{-1}$ is reported for this ion [28, 29]. β_1^2, β_2^2, and γ^2 are the coefficients of the molecular orbitals of the d electrons.

The parallel and perpendicular components of the hyperfine interaction $A_{\parallel}$ and $A_{\perp}$ are related to the molecular orbital coefficients by the expressions [25–31]

$$A_{\parallel} = -P\left[\kappa + \frac{4}{7}\beta_2^2 + (g_e - g_{\parallel}) + \frac{3}{7}(g_e - g_{\perp})\right], \quad (5)$$

$$A_{\perp} = -P\left[\kappa - \frac{2}{7}\beta_2^2 + \frac{11}{14}(g_e - g_{\perp})\right]. \quad (6)$$

Table 2. Fermi contact terms and molecular orbital coefficients of the vanadyl complexes in various lattices.

Lattice	κ	β_2^2	Reference
$Na_3C_6H_5O_7{\cdot}2H_2O$	0.72	0.93	Present work
$Na_3C_6H_5O_7{\cdot}5H_2O$	0.78	0.90	[13]
$(NH_4)_3C_6H_5O_7$	0.72	0.90	[14]
$K_3C_6H_5O_7{\cdot}H_2O$	0.71	0.94	[15]
$Ca(pic)_2(bipy)_2$	0.77	0.95	[31]
$K_2C_2O_4{\cdot}H_2O$	0.70	0.96	[34]
$VO(H_2O)_5^{2+}$	0.83	1.00	[35]

The degree of distortion can be estimated from the Fermi contact terms κ and the P parameter, which are related to the radial distribution of the wave function of the ions, given as $P = g_e g_N \beta_e \beta_N \langle \boldsymbol{r}^{-3} \rangle$. The Fermi contact term is directly related to the isotropic hyperfine coupling and represents the amount of unpaired electron density at the nucleus, where P is the dipolar interaction constant between the magnetic moment of the electron and the vanadium nucleus.

Neglecting the second order effects and taking negative values for $A_{\parallel}$ and $A_{\perp}$, the P values are calculated from (7) and are given in Table 1 [33]

$$P = \frac{7(A_{\parallel} - A_{\perp})}{6 + (3/2)(\lambda/\Delta_{\parallel})}. \quad (7)$$

The isotropic and anisotropic (g and A) parameters are calculated from (8) and (9)

$$g_{iso} = (2g_{\perp} + g_{\parallel})/3, \quad (8)$$

$$A_{iso} = (2A_{\perp} + A_{\parallel})/3. \quad (9)$$

Using these equations with (5) and (6) one gets

$$\kappa = \frac{A_{iso}}{P} - (g_e - g_{iso}), \quad (10)$$

and the Fermi contact parameter is calculated. Using P and κ in (5) and (6), β_2^2, which is the covalancy ratio of the V=O bonds, is calculated. Using these values with (3) and (4), β_1^2 and γ^2 are evaluated. All the parameters are given in Table 1. From Table 1, the wave functions and expression for the spin-Hamiltonian parameters in the present study are same as those for $VO(H_2O)_5^{2+}$ complexes. Table 2 compares the κ and β_2^2 obtained for this lattice with other lattices. The value of β_2^2 should be unity as the orbital is nonbonding as in the case of pure $VO(H_2O)_5^{2+}$ complexes

[13, 25, 27, 32]. The deviation of β_2^2 from unity usually represents the degree of admixture of the ligand orbitals and increase in the degree of the covalancy. β_2^2, found in this work, clearly indicates that the bonding is nearly ionic and represents poor π bonding of the ligands. However, κ value in the present study is smaller than in most of the other lattices and indicates the mixing of the 4s orbital into the d_{xy} orbital. It may be due to a low symmetry ligand field.

The parameters $1-\beta_1^2$ and $1-\gamma^2$ are the measures of the covalency. The first term gives an indication of the influence of σ bonding between the vanadium atom and equatorial ligands, the second indicates the influence of π bonding between the vanadium ion and the vanadyl oxygen. In this work, γ^2 is less than β_2^2 for all the complexes, indicating that the in plane σ bonding is more covalent than the in plane π bonding.

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