An EPR and Optical Study of VO^{2+} in Bis (Glycine) Cadmium Chloride Single Crystals

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Results of EPR and optical studies of VO^{2+} doped in bis (glycine) cadmium(II) chloride, belonging to a third site as a substitutional one are reported. The spin Hamiltonian parameters obtained for the site are $g_{zz} = 1.9159$, $g_{yy} = 1.9695$, $g_{xx} = 1.9853$, $A_{zz} = 210.4$ G, $A_{yy} = 109.8$ G, and $A_{xx} = 107.0$ G. By correlating the EPR and spectral data, the molecular orbital bonding parameters have been evaluated.

Key words: Crystal Growth; Electron Paramagnetic Resonance; Bonding Parameters.

1. Introduction

The crystal structure of amino acids is of great interest since they serve as model compounds for the study of macromolecules. Metal complexes of amino acids and related systems have been investigated to understand the sequence of coordination in the organometallic systems which are of major interest in nutritional and medical technology [1]. In order to understand the behaviour of many inorganic complexes, their EPR spectra have been reported [2 – 11]. EPR and bonding parameters have already been reported for site A and site B [12]. The present study reveals the bonding parameters of the third site C of VO^{2+} ions in its surroundings.

2. Experimental

2.1. General

Glycine and cadmium chloride (BGCdCl) constituents were mixed in stoichiometric proportions and crystals were grown by slow evaporation of the aqueous saturated solution along with 0.5% by weight of $VOCl_2$ at room temperature. Good crystals in the form of elongated hexagonal pillars could be easily obtained. Colourless single crystals of BGCdCl are used for EPR studies. The spectra were recorded at room temperature on a Varian E-112 EPR spectrometer operating at the X band with 100 kHz magnetic field modulation. The crystal was rotated about the three orthogonal crystal axes a^*, b, and c and the measurements were taken for every 5° or 10° rotation.

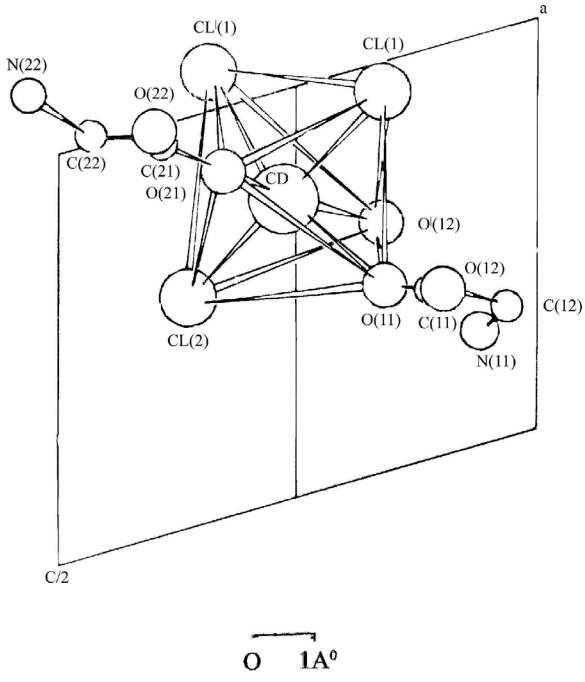

Fig. 1. A view of the octahedral coordination around a cadmium atom looking along the crystal *b*-axis. Projection is on the *ac* plane.

2.2. Crystal Structure

BGCdCl crystallizes in a tetra molecular monoclinic unit cell of the dimensions $a = 8.17$ Å, $b = 8.91$ Å, $c = 13.62$ Å and $\beta = 107°(9')$ in the space group $P2_1/n$. There is only one cadmium atom in the asymmetric

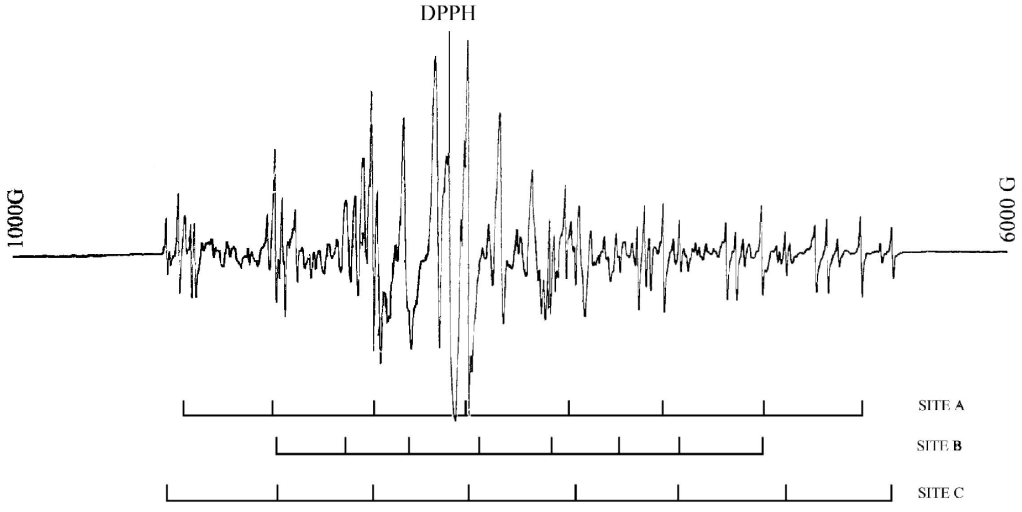

Fig. 2. EPR spectrum of VO^{2+} ions in BGCdCl when the magnetic field is parallel to the *c*-axis in the *cb* plane.

part of the unit cell, and it is coordinated to six nearest neighbours, the coordination polyhedron being a distorted octahedron. A view of the cadmium coordination looking along the *b*-axis of the crystal is shown in Figure 1. The octahedron is occupied by three oxygen and three chlorine atoms. The Cd–Cl distance ranges from 2.46 Å to 2.59 Å, and the Cd–O distance varies from 2.249 Å to 2.376 Å. One of the glycine molecules bridges two cadmium atoms bidentally through O(11) and O(12).

3. Results and Discussion

A typical EPR spectrum of VO^{2+} in a BGCdCl single crystal is given in Figure 2. It shows the EPR spectrum of VO^{2+} ions in BGCdCl when the magnetic field is parallel to the *c*-axis in the *cb* plane. The EPR spectrum consists of many intense lines with a complex structure. Among many sites, only the site C is presented here. The BGCdCl EPR spectrum was completely analyzed and could be successfully extracted up to three sites by A, B, and C. Other lines could not be followed in many orientations in all the three planes because of their weak intensity and overlapping nature. The sites A (interstitial) and B (substitutional) are already reported in [12]. The observed groups of eight lines are shown in Figure 2. Generally one could observe eight hyperfine lines for a VO^{2+} due to the interaction of the electron spin ($S = 1/2$) with the nuclear spin ($I = 7/2$), since the VO^{2+} ion is in its $3d^3$ configuration. Single crystal angular variation spectra are obtained as shown in Figure 3. The observed spectra have been fitted to an orthorhombic spin Hamiltonian

$$\begin{aligned} H = {} & \beta(g_{zz}H_zS_z + g_{yy}H_yS_y + g_{xx}H_xS_x) \\ & + (A_{zz}I_zS_z + A_{yy}I_yS_y + A_{xx}I_xS_x), \end{aligned} \tag{1}$$

where the terms have their usual meaning [13]. The *g* value variation for site C has been fitted with the following expression [14]:

$$g^2_{a^*}(\theta) = \alpha + \beta\cos 2\theta + \gamma\sin 2\theta, \tag{2}$$

where

$$\begin{aligned} 2\alpha &= g^2_{\max\,\mathrm{i}} + g^2_{\min}, \\ 2\beta &= (g^2_{\max\,\mathrm{i}} - g^2_{\min})\cos 2\theta_{\max\,\mathrm{i}}, \\ 2\gamma &= (g^2_{\max\,\mathrm{i}} - g^2_{\min})\sin 2\theta_{\max\,\mathrm{i}}, \end{aligned} \tag{3}$$

and $g_{\max\,\mathrm{i}}$ and $g_{\min}$ are the maximum and minimum *g* values in the plane of rotation (*bc* plane) and $\theta_{\max\,\mathrm{i}}$ is the angle from *b*-axis at which the $g_{\max\,\mathrm{i}}$ occurs. $g^2_{a^*}(\theta)$ is the *g* value variation when the crystal is rotated about the a^*-axis. Similarly, the $g^2_b(\theta)$ and $g^2_c(\theta)$ variations have been fitted with the experimental values. The variations in the hyperfine coupling constant *A* have been fitted with the following expression [15]:

$$\begin{aligned} (gA)^2_{a^*}(\theta) = {} & (gA)^2_{bb}\cos^2\theta + (gA)^2_{cc}\sin^2\theta \\ & + (gA)^2_{bc}\sin 2\theta, \end{aligned} \tag{4}$$

where $(gA)_{bb}$ and $(gA)_{cc}$ are the (gA) values along the *b*- and *c*-axes, respectively. $(gA)_{bc}$ represents cross

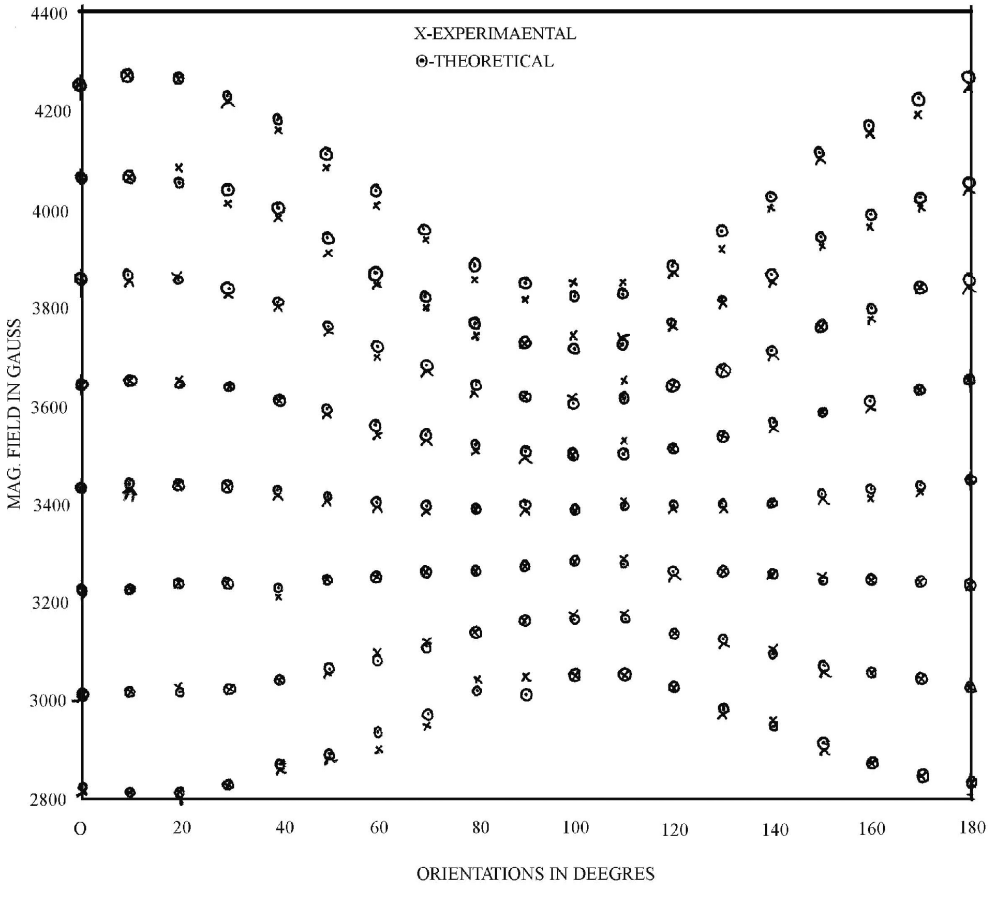

Fig. 3. The angular variation spectra of BGCdCl.

Table 1. Spin Hamiltonian parameters of VO^{2+} in BGCdCl for the site C; the direction cosines of the *g* and *A* tensor values have been given with respect to the a^*-, *b*- and *c*-axes.

		I	*M*	*N*
g_{zz}	1.9159	0.1962	0.1561	0.9681
g_{yy}	1.9695	0.4660	0.8538	−0.2321
g_{xx}	1.9853	1.9853	−0.4967	−0.0948
A_{zz}	210.4 G	0.2130	0.1860	0.9592
A_{yy}	109.8 G	0.3554	0.09082	−0.2505
A_{xx}	107.0 G	−0.9177	0.3751	0.1311

Table 2. Comparison of VO^{2+} ions direction cosines belonging to substitutional site B and C with the cadmium oxygen orientation with respect to the a^*-, *b*-, and *c*-axes of the BGCdCl crystal.

Crystal data	Metal-oxygen distance	Direction cosine *l*	*m*	*N*
Cd-O(11)*	2.3904	0.3839	−0.4790	0.7894
Cd-O(11)	2.3750	0.3678	0.4821	0.7952
EPR data	*g* Value			
B site g_{zz}	1.922	0.3068	−0.26621	0.9136
C site g_{zz}	1.9159	0.1962	0.1561	0.9681

terms in the *bc* plane, to be determined from the experimental angular variation plot.

The experimental points agree with the theoretical points, for A variation in site C, as seen in Figure 3. The diagonalization procedure was carried out following the standard procedure given by Schonland [14] in the analysis of EPR spectra, for obtaining the principal *g* and *A* tensors which are given in Table 1. The EPR line of VO^{2+} ions belonging to the site C has entered into substitutional cadmium location. This assumption is supported by crystal structure data. When comparing the g_{zz} direction cosines with the Cd-O(11) direction in the octahedral coordination, the direction cosine of the site C will be along Cd-O(11), as in Table 2. The substitutional site B, which was reported [12] earlier, is also shown in Table 2 for comparison.

Using EPR and optical data, the VO^{2+} bonding parameters are determined. The spin Hamiltonian parameters are related to the molecular orbital parameters

by the following relations [16]:

$$g_{\parallel} = g_e \left[1 - \frac{4\lambda\alpha^2}{E(b_2 \rightarrow b_1^*)}\right], \quad (5)$$

$$g_{\perp} = g_e \left[1 - \frac{\lambda\gamma^2}{E(b_2 \rightarrow e_\pi^*)}\right], \quad (6)$$

where $g_{\parallel}$ and $g_{\perp}$ are experimental data, $g_e = 2.0023$, λ is the spin orbit coupling constant of the ion and is a function of the effective nuclear charge. For more than half-filled shells λ is negative, and for less than half-filled shells it is positive. For the VO^{2+} ion λ is chosen [17–19] as 175 cm^{-1}. α^2 and γ^2 are the σ and π covalent bond coefficients. $E(b_2 - b_1^*)$ and $E(b_2 - e_\pi^*)$ are the optical absorption values for the first and second excited energy levels. The optical absorption spectrum was recorded for BGCdCl:VO^{2+} single crystals using a Cary 14 optical absorption spectrometer. Two broad peaks at 11,765 cm^{-1} and 15,625 cm^{-1} were assigned to the transition energies corresponding to $E(b_2 - e_\pi^*)$ and $E(b_2 - b_1^*)$, respectively. The closer the values of α^2 and γ^2 to unity, the weaker the covalent rates. $(1 - \alpha^2)$ is a measure of the influence of the σ bonding between a vanadium atom and equatorial ligands, while $(1 - \gamma^2)$ is the influence of the π bonding between a vanadium and axial oxygen atom. The estimated values are presented in Table 3. Since $(1 - \gamma^2)$ is greater than $(1 - \alpha^2)$ for a site C, the π bonding between the axial ligands is stronger than the equatorial ligand to vanadium σ bonding as that of site B. However, the strength of $(1 - \alpha^2)$ for site B is larger than that for site C. This indicates weaker equatorial σ bonding in the case of site C. Also, axial π bonding for site C is weaker than that for site B, as seen from Table 3. From the general spin Hamiltonian applying second order perturbation technique [16, 18] the following expressions relating EPR data, optical data and bonding parameters for the VO^{2+} ion could be obtained:

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

$$A_{\perp} = P\left[-K + \frac{2}{7}\beta_2^{*2} - \frac{11}{14}(g_e - g_{\perp})\right], \quad (8)$$

$$g_e - g_{\parallel} = \frac{8\beta_1^{*2}\beta_2^{*2}\lambda}{E(b_2 \rightarrow b_1^*)}, \quad (9)$$

$$g_e - g_{\perp} = \frac{2\beta_2^{*2}e_\pi^{*2}\lambda}{E(b_2 \rightarrow e_\pi^*)}, \quad (10)$$

Table 3. Molecular orbital coefficients and covalent factors of VO^{2+} ions in the BGCdCl lattice.

Lattice	β_2^{*2}	e_π^{*2}	β_1^{*2}	K	$1-\alpha^2$	$1-\gamma^2$
Site A	0.45	0.95	1.00	1.00	0.33	0.43
Site B	0.70	0.90	1.00	1.00	0.32	0.16
Site C	0.7129	1.00	1.00	0.9658	0.0357	0.1678

where $P = 2.0023\, g_N\, \beta_e \beta_N \langle r^{-3} \rangle_{avg}$ is the dipole-dipole interaction term between the electron and the nucleus. β_2^{*2} is the antibonding orbital for the ground state b_2 or d_{xy} orbital, K is the Fermi contact term. e_π^{*2} and β_1^{*2} are the antibonding coefficients for the e_π^* and b_1^{*2} excited levels. P was assumed [20, 21] to be 0.0128 cm^{-1}. In (9) and (10) the electron transition energy level namely ground excited states e_π^*, b_1^* shown are the same as that of the energy transition, as shown in (5) and (6). $b_2 \rightarrow b_1^*$ means that the electric dipole undergoes transition between these two energy levels. It is also similar for $b_2 \rightarrow e_\pi^*$ energy levels. Here $\beta_2^{*2} = 0.7129$ corresponds to 71% of antibonding characteristics. The parameter K indicates extreme sensitivity to the deformations of the electron orbital of the central vanadium ion. The value of K (0.9658) indicates that the unpaired electron spin polarization towards the vanadyl nucleus is roughly 4%. As for sites A and B, site C exceeds unity in the value of β_1^{*2}. β_1^{*2} is a measure of inplane σ bonding.

Since this value is larger than 1, the σ bonding is large, i. e. the vanadyl 3d orbital and O(11) are tightly bound. This means that the b_1^* energy level is lowered sufficiently towards the ground state b_2 which is a mixture of the β_1^* excited level. Here $\beta_1^{*2} = 1.3521$ is taken as maximum 1. Similarly $e_\pi^{*2} = 1.1745$ is also taken as 1, which indicates that the ground state b_2 level is again admixed by the first excited state e_π^{*2}. Thus, this excited antibonding orbital level is also lowered towards the b_2 level. Such an energy level diagram is given in Figure 4.

4. Conclusion

As discussed above, the third site C has entered substitutionally in the cadmium atom location. The VO^{2+} ion impurity with 0.5% by weight is doped with BGCdCl. It occupies the cadmium location and orients along the O(11) direction. The bonding parameter of site C is similar to that of other substitutional sites B except for the $(1 - \alpha^2)$ value. This smaller value indicates that the equatorial σ bonding VO^{2+} ion with the O(11) atom is weak. The axial π bonding for site C is also weaker than site B.

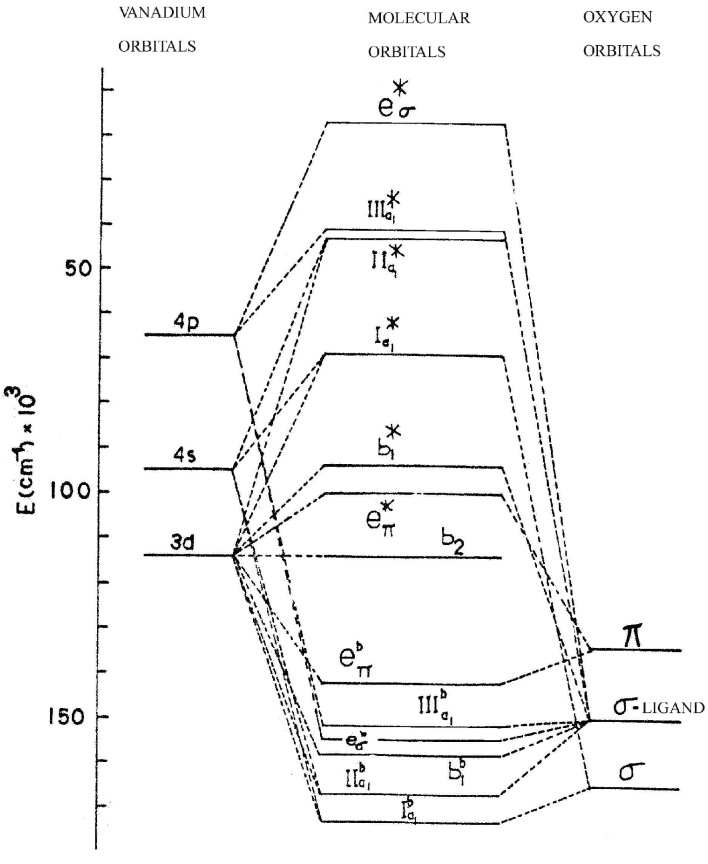

Fig. 4. Vanadium-oxygen molecular orbital energy level scheme derived by Ballhausen and Gray [17] from semi-empirical molecular orbital calculations. The levels are drawn to scale.

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