EPR Study of VO^{2+} Doped Diammonium Tricadmium Tetrakis (Sulfate) Pentahydrate $[(NH_4)_2Cd_3(SO_4)_4{\cdot}5H_2O]$ Single Crystals

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Electron paramagnetic resonance (EPR) studies are carried out on vanadyl (VO^{2+}) ions in diammonium tricadmium tetrakis (sulfate) pentahydrate single crystals at room temperature. The EPR spectra of a single crystal exhibit resonance signals characteristic to VO^{2+} ions. The analysis of EPR spectra indicates that the VO^{2+} ions in single crystals show two magnetically inequivalent VO^{2+} sites in distinct orientations occupying substitutional positions in the lattice and showing very high angular dependence. They form in octahedral coordination with tetragonal compression with C_{4v} symmetry. The spin Hamiltonian parameters are determined, and these parameters have been used to estimate the bonding coefficients of the VO^{2+} ion in a diammonium tricadmium tetrakis (sulfate) pentahydrate lattice. The parallel and perpendicular components of axially symmetric **g** and hyperfine (**A**) tensors are evaluated and the results are discussed and compared with previous reports.

Key words: EPR; ESR; Vanadyl Ion; Single Crystal.

1. Introduction

The electron paramagnetic resonance spectroscopy is one of the suitable techniques for studying transition metal complexes which have at least one unpaired electron on their d orbitals. It is also useful for studying the bonding of metals to organic and inorganic ligands [1, 2]. Paramagnetic VO^{2+} ions with $3d^1$ configuration are often used as a probe in crystalline materials reflecting the local symmetry and the structural properties of the host. Therefore, the EPR spectra of VO^{2+} ions in different diamagnetic lattices have been studied by many workers to get information about the structure, dynamics, and environment of the host lattices [3 – 9]. The behaviour of an unpaired electron in VO^{2+} complexes is dominated by the strong V=O bonding and it is always in a non-degenerate state leading the EPR spectra. As a result, most of the complexes form distorted octahedral sites (C_{4v}) compressed along the z-axis and both g and A values are found to be axially symmetric [10 – 12].

Sulfates are important as well as in biological and medical applications, therefore its derivatives and their metal complexes are widely studied. Because of their wide applications in technology, impurities in sulfate crystals, including divalent and trivalent metal ions, are introduced and investigated to show the effects on optical, electrical, and other physical properties [13 – 15]. EPR studies of VO^{2+} in some sulfate complexes have also been reported [16 – 20]. Since there is no report in literature on the EPR studies of VO^{2+} doped in diammonium tricadmium tetrakis (sulfate) pentahydrate single crystals to our knowledge, we have undertaken the aforesaid investigation.

2. Experimental

An aqueous solution of $(NH_4)_2SO_4$ and $3CD(SO_4){\cdot}8H_2O$ with equal molarity is prepared. About one percent of $VOSO_4{\cdot}3H_2O$ is added to the solution as impurity. The solution is left to evaporation at room temperature slowly. Well developed single crystals of diammonium tricadmium tetrakis (sulfate) pentahydrate (DATTS) are obtained in about one week. DATTS single crystals belong to the monoclinic system, space group $P2_1/c$ [21], and contain four molecules in a unit cell. The unit cell parameters are: $a = 19.678$ Å, $b = 9.872$ Å, $c = 10.073$ Å, and $\beta = 102.097\,^\circ$.

The EPR spectra are recorded on a Varian E-109 Century Series X band EPR spectrometer with a magnetic field modulation frequency of 100 kHz. The single crystal is mounted on a goniometer and the spectra are recorded at room temperature in three

Table 1. Principal values and direction cosines of the **g** and **A** tensors of VO^{2+} doped $(NH_4)_2Cd_3(SO_4)_4{\cdot}5H_2O$ single crystals. $\Delta g = \pm 0.005$ and $\Delta A = \pm 2$ G.

Site	**g**	Direction cosines			**A**(G)	Direction cosines		
		a^*	b	c		a^*	b	c
I	$g_x = 1.988$	0.781	0.621	0.062	$A_x = 79$	0.741	0.670	0.035
	$g_y = 1.990$	0.189	−0.331	0.924	$A_y = 75$	0.252	−0.326	0.911
	$g_z = 1.950$	−0.595	0.711	0.376	$A_z = 197$	−0.622	0.667	0.411
II	$g_x = 1.994$	0.760	−0.650	0.012	$A_x = 77$	0.703	−0.705	−0.091
	$g_y = 1.992$	0.238	0.296	0.925	$A_y = 75$	0.344	0.226	0.911
	$g_z = 1.943$	0.605	0.700	−0.379	$A_z = 199$	0.622	0.672	−0.402

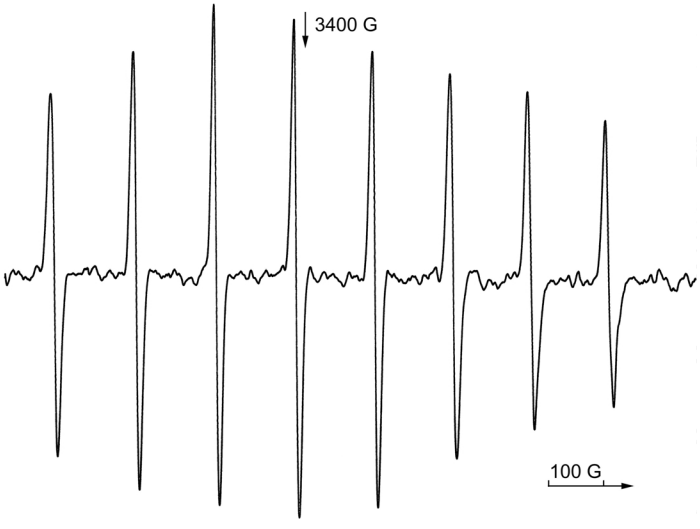

Fig. 1. EPR spectrum of VO^{2+} doped DATTS single crystals, the magnetic field is along the b-axis.

mutually perpendicular planes (a^*c, bc, and a^*b), respectively, with 10° intervals, where the a^*-axis is perpendicular to the crystallographic b and c-axes. An EPR spectrum of a powder sample is also recorded at room temperature. A diphenylpicrylhydrazyl sample ($g = 2.0036$) is used as a reference to correct the g values.

3. Results and Discussions

The V^{4+} ion has a $3d^1$ electronic configuration and is found as VO^{2+}. It is paramagnetic and has eight hyperfine lines originating from the ^{51}V isotope with a natural abundance of 99.8% and a nuclear spin of $I = 7/2$. The EPR spectrum of a VO^{2+} doped DATTS single crystal taken at room temperature is shown in Figure 1, with the magnetic field along the b-axis. The spectrum consists of two sets of eight hyperfine lines, and in this orientation both sites demonstrate the monoclinic crystal symmetry. Figure 2 shows line positions and fitted curves, when the magnetic field is in a^*c, bc- and a^*b-plane, respectively. Only one site is observed in the a^*c-plane as expected for the monoclinic symmetry and two sites are observed in two other planes. Both of the sites have the same intensity and therefore the same populations. The g^2 variation of a specific line with respect to the rotation angle in each plane is fitted to the expression,

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

where i, j, k, and θ represent x-, y-, z-axes, and the rotation angle, respectively, which is used to resolve the spectra [22].

The EPR spectra of vanadyl complexes can be satisfactorily explained in terms of an unpaired electron ($S = 1/2$) coupled with a vanadium nucleus ($I = 7/2$). The spectra can be described in terms of a spin-Hamiltonian of the form

$$\mathcal{H} = \beta_e \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}, \quad (2)$$

which includes only electronic Zeeman and hyperfine interactions, respectively [22]. Quadrupol and nuclear Zeeman terms are not included in (2) due to the smaller

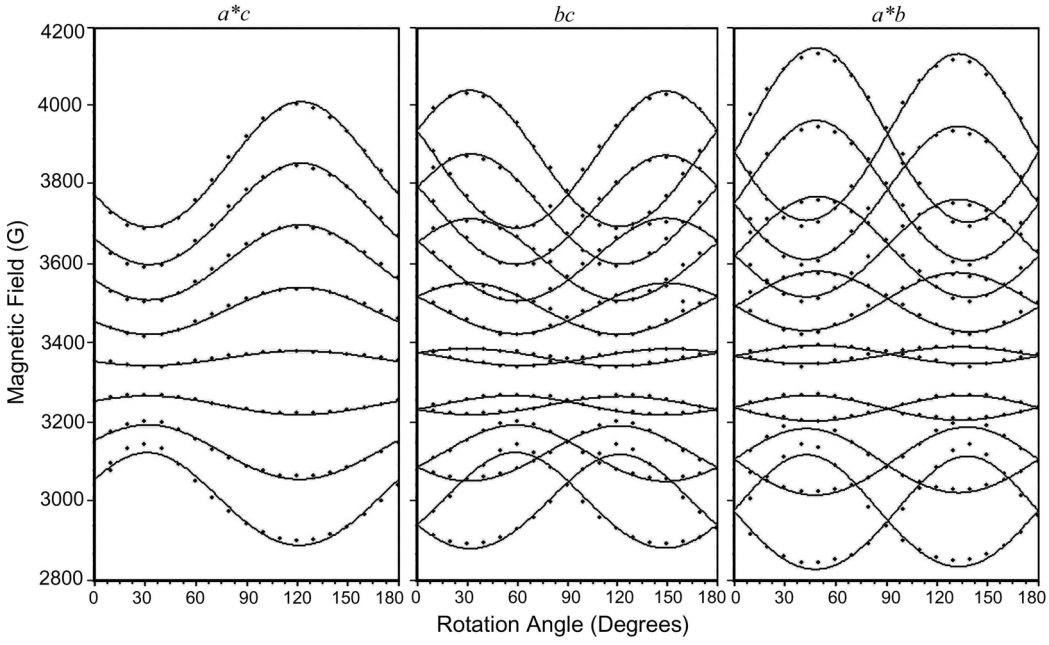

Fig. 2. Angular variations of hyperfine lines in the VO^{2+} doped DATTS single crystals.

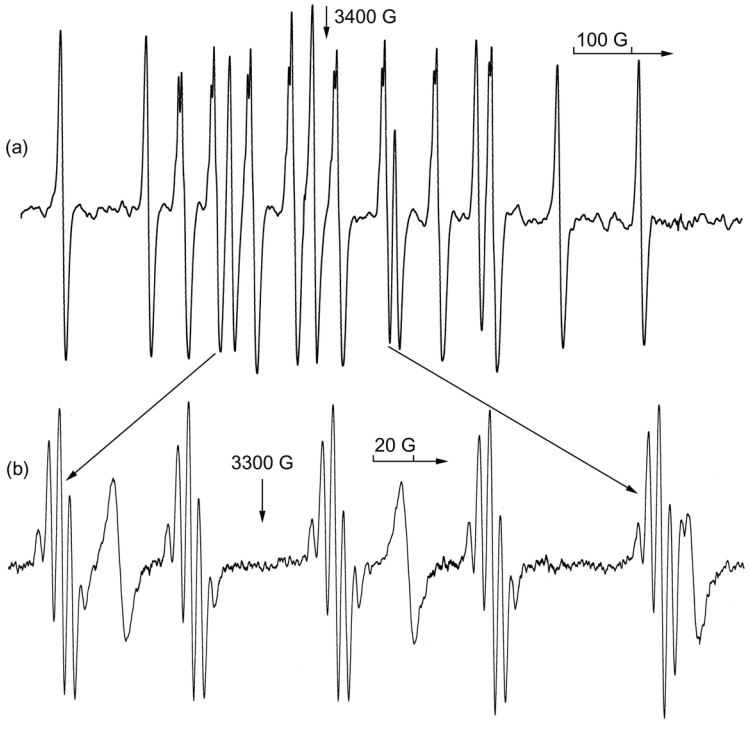

Fig. 3. (a) EPR spectrum of a VO^{2+} doped DATTS single crystal at room temperature, with the magnetic field in the a^*c-plane and an angle of 60° to the a^*-direction, (b) recorded in a small scan field in the same direction to show the proton super hyperfine splitting caused by two water molecules.

magnitudes of these interactions. The spin orbit interaction is intrinsic in the g value. In order to find the g and A values, we have used an iterative numerical technique. After the calculations, **g** and **A** tensors are constructed and digonalized to find principal g and A values. The results are given in Table 1. Both sites are

Table 2. Principal g, hyperfine (A) values, and molecular orbital coefficients for vanadyl ion complexes in DATTS single crystals compared with the literature. A and P are in units of 10^{-4} cm^{-1}.

Complex	Site	$g_\parallel$	$g_\perp$	g_{iso}	$A_\parallel$	$A_\perp$	A_{iso}	P	κ	β_2^2	References
DATTS	I	1.950	1.989	1.976	184.2	72	109.4	131	0.86	0.99	This work
	II	1.943	1.993	1.976	186	71	109.2	134	0.84	0.98	This work
$NaHC_2O_4{\cdot}H_2O$		1.931	1.999	1.976	183.2	65.4	104.6	137	0.79	1.00	[9]
$(NH_4)HC_2O_4{\cdot}0.5H_2O$		1.947	1.997		194.4	63.5		152	0.72	1.00	[26]
$C_6H_4AsNO(H_2O)_2$		1.919	1.995	1.969	191.2	76.8	113.4	144	0.81	1.00	[37]

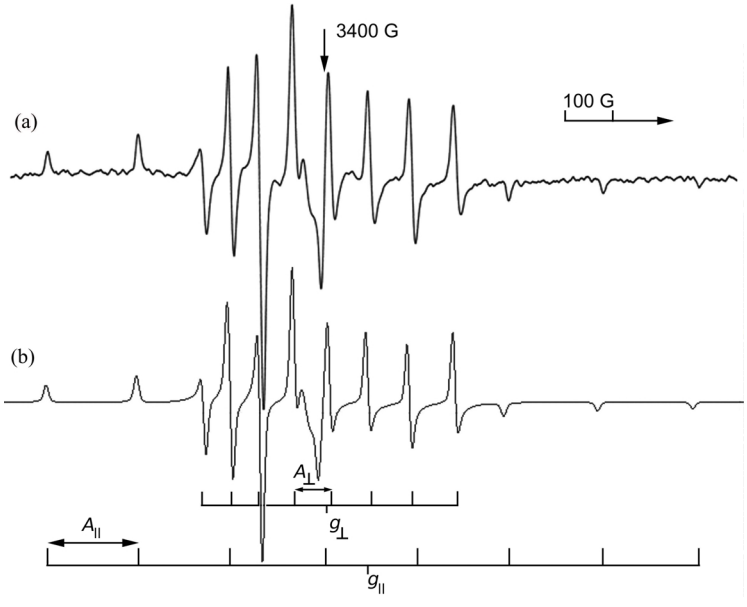

Fig. 4. (a) Powder sample EPR spectrum of VO^{2+} doped DATTS crystals, (b) computer simulation of the spectrum.

nearly axially symmetrical. There exist two magnetically inequivalent and chemically equivalent sites for a DATTS single crystal, because principal g and A values of two sites are equal within the experimental error.

Figure 3 shows the EPR spectrum of a VO^{2+} doped DATTS single crystal at room temperature, with the magnetic field in the a^*c-plane and an angle of 60° from the a^*-direction. Figure 3a includes 16 hyperfine lines because of the two VO^{2+} sites in the crystal. Super hyperfine splitting which originates from two nearby water molecules are shown in Figure 3b. Four equivalent hydrogen atoms of nearby water molecules splits each of the VO^{2+} lines equally with the value 3.4 G and intensity distribution 1 : 4 : 6 : 4 : 1. This super hyperfine splitting in VO^{2+} doped sulfate complexes is also observed in literature [23 – 25]. Figure 3b shows the expended part of the spectrum in Figure 3a indicated with arrows. In DATTS single crystals, each Cd^{2+} ion forms an octahedral environment with six oxygen atoms, four of them belong to sulfate ions and the next two oxygen atoms belong to two water molecules. The two Cd atoms (Cd1 and Cd2) share one of the five water molecules existing in the crystal whereas the other four water molecules are not shared with Cd atoms. Consequently, water molecules, coordinated to the Cd3 atom, are not shared by other two Cd atoms [21]. From these result we conclude that the VO^{2+} ions substitute the Cd3 ions. Figure 4a shows the powder EPR spectrum, recorded at room temperature. The computer simulation of this spectrum is shown in Figure 4b. We have used the average values of Table 1 for the simulation, given as $g_\perp = 1.991$, $g_\parallel = 1.947$, $a_\perp = 76.5$ G, and $a_\parallel = 198$ G. The powder and the simulated spectra also indicate that these sites are chemically equivalent.

An octahedral complex with a tetrahedral distortion has $g_e > g_\perp > g_\parallel$ and $|A_\parallel| > |A_\perp|$ [9, 26 – 29]. The deviation of the $g_\parallel$ and $g_\perp$ values from the g_e value free electron is generally denoted by $\Delta g_\parallel$ and $\Delta g_\perp$, respectively. The $\Delta g_\parallel / \Delta g_\perp$ ratio that measures the tetragonality of the VO^{2+} sites is calculated to be 4.9, which is greater than unity and therefore it can

be said that the VO^{2+} ions environment is tetragonaly distorted.

The parallel and perpendicular components of the hyperfine interaction, $A_\parallel$ and $A_\perp$ are related to the molecular orbital coefficients by the following expressions [30–37]:

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

$$A_\perp = -P\left[\kappa - \frac{2}{7}\beta_2^2 + \frac{11}{14}(g_e - g_\perp)\right], \quad (4)$$

where $P = g_e g_n \beta_e \beta_n \langle r^{-3}\rangle$ is the dipole-dipole interaction constant of the magnetic moments of electron and vanadium nucleus [38], κ is the Fermi contact term indicating the d-orbital population for unpaired electrons, β_2 is the in-pane π-bonding coefficient of a vanadium ion with the ligands. g_e and g_n are the g values of electron and nucleus, β_e and β_n are the Bohr magnetons of electron and nucleus, respectively, and r is the electron radius.

Neglecting the second order effects and taking the negative values for $A_\parallel$ and $A_\perp$, P values are calculated from the following equation and the results are given in Table 2 [39]:

$$P = \frac{7(A_\parallel - A_\perp)}{6 + (3/2)(\lambda/\Delta_\parallel)}, \quad (5)$$

where λ (= 170 cm^{-1} [32, 33]) is the spin-orbit coupling constant of the vanadium ion and $\Delta_\parallel$ is the $^2B_{2g} \rightarrow {}^2B_{1b}$ electronic transition of the vanadium d-electrons. The second term may be neglected in the dominator in (5). Isotropic g and A values are found as:

$$g_{iso} = \frac{2g_\perp + g_\parallel}{3}, \quad (6)$$

$$A_{iso} = \frac{2A_\perp + A_\parallel}{3}. \quad (7)$$

Using (5), (6), and (7), the Fermi contact term is calculated by using the following formula:

$$\kappa = -\frac{A_{iso}}{P} - (g_e - g_{iso}). \quad (8)$$

After calculating P and κ and inserting into (3) and (4), β_2^2 is obtained. All parameters are given in Table 2. For a free electron, the P value is $160 \cdot 10^{-4}$ cm^{-1} [1, 40]. The calculated values in DATTS (Table 2) are smaller than this value. By comparing the calculated values of the P parameter it is found, that the complex has a fairly covalent nature. 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 covalency. Because of the nearly equality of unity of β_2^2, in-plane π-bonding is part of the ionic character and the ligands have poor π-bonding. Because κ is lower than β_2^2, the delocalization of the electron is not great and the in-plane π-bonding ability of the ligand is poor.

4. Conclusion

The EPR spectra of VO^{2+} ions doped in DATTS single crystals have been studied at room temperature. The EPR spectra show a well-resolved hyperfine structure pattern. The angular variation of the EPR spectra reveals the presence of two magnetically inequivalent vanadyl complexes. The detailed EPR analysis shows that the vanadyl ions occupy the substitutional positions of the Cd^{2+} ions in the crystal lattice. The spin-Hamiltonian parameters are evaluated and the **g** and **A** tensors are found to have an axial symmetry. For both sites, the $g_\parallel < g_\perp < g_e$ trend shows the presence of an unpaired electron in the d_{xy} orbital. The results show that for two VO^{2+} sites are $g_\parallel < g_\perp < g_e$ and $|A_\parallel| > |A_\perp|$. So it is confirmed that the VO^{2+} ions in DATTS are in octahedral coordination with tetragonal distortion.

[1] B. D. P. Raju, K. V. Narasimhulu, N. O. Gopal, and J. L. Rao, J. Phys. Chem. Solids **64**, 1339 (2003).

[2] R. Kripal, M. Mauryaa, and H. Govind, Physica **392b**, 281 (2007).

[3] S. Dhanuskodi and A. P. Jeyakumari, Spectrochimica Acta **57a**, 971 (2001).

[4] Y. Yerli, F. Köksal, and A. Karadag, Solid State Sci. **5**, 1319 (2003).

[5] R. Kripal and I. Mishra, Spectrochimica Acta **72**, 538 (2009).

[6] B. Karabulut, İ. İlkin, and R. Tapramaz, Z. Naturforsch. **60a**, 95 (2005).

[7] R. Bıyık and R. Tapramaz, Z. Naturforsch. **60a**, 669 (2004).

[8] M. Venkateshwarlu and T. B. Rao, Solid State Commun. **82(10)**, 837 (1992).

[9] B. Karabulut and A. Tufan, Spectrochimica Acta **65a**, 285 (2006).
[10] S. Kasturirengan and S. Soundararajan, J. Magn. Reson. **19**, 357 (1975).
[11] R. Tapramaz, B. Karabulut, and F. Koksal, J. Phys. Chem. Solids **61**, 1367 (2000).
[12] P. Chand, R. M. Krishna, J. L. Rao, and V. J. Lakshman, Radiat. Effects and Defects in Solids **127**, 245 (1993).
[13] N. M. Zain and A. K. Arof, Materials Sci. Eng. **52b**, 40 (1998).
[14] K. Kirubavathi, K. Selvaraju, R. Valluvan, and S. Kumararaman, Mater. Lett. **61**, 4173 (2007).
[15] P. Williams, E. Keshavarz-Moore, and P. Dunnill, Enzyme and Microbial Technology **30**, 354 (2002).
[16] K. V. Narasimhulu and J. L. Rao, Spectrochimica Acta **53a**, 2605 (1997).
[17] K. Vasantha, P. A. Angeli Mary, and S. Dhanuskodi, Spectrochimica Acta **58a**, 311 (2002).
[18] C. Shiyamala, B. Natarajan, R. V. S. S. N. Ravikumar, and P. S. Rao, Physica Scripta **74**, 549 (2006).
[19] J. L. Rao and K. Purandar, Solid State Commun. **33(3)**, 363 (1980).
[20] S. K. Misra, J. Sun, and X. Li, Physica B: Condensed Matter **168**, 170 (1991).
[21] D. Swain and T. N. G. Row, Acta Cryst. **62e**, i226 (2006).
[22] B. Karabulut and R. Tapramaz, Radiat. Phys. Chem. **55**, 331 (1999).
[23] S. K. Misra and J. Sun, Physica B **162**, 331 (1990).
[24] S. K. Misra and J. Sun, Phys. Rev. B **42(13)**, 8601 (1990).
[25] S. K. Misra and J. Sun, Phys. Rev. B **44(18)**, 10333 (1990).
[26] B. Karabulut and A. Tufan, Spectrochimica Acta **65a**, 742 (2006).
[27] A. K. Bandyopadhyay, J. O. Isard, and S. Parke, J. Phys. D: Appl. Phys. **11**, 2559 (1978).
[28] A. Abragam and B. Bleney, Electron Paramagnetic Resonance of Trasition Ions, Calendron Press Oxford 1970, p. 175.
[29] A. Murali, J. L. Rao, and A. V. Subbaiah, J. Alloys Comp. **257**, 96 (1997).
[30] R. P. S. Chakradhar, A. Murali, and J. L. Rao, Physica **293b**, 108 (2000).
[31] V. P. Seth, S. Gupta, A. Jindal, and S. K. Gupta, J. Noncryst. Solids **162**, 263 (1993).
[32] R. Muncaster and S. Parke, J. Noncryst. **24**, 399 (1977).
[33] C. R. Balhausen and H. B. Gray, Inorg. Chem. **1**, 111 (1962).
[34] D. Kivelson and S. K. Lee, J. Chem. Phys. **41(7)**, 1896 (1964).
[35] M. Narayana, S. G. Sathyanarayana, and G. S. Sastry, Mol. Phys. **31(1)**, 203 (1973).
[36] D. Pathinettam Padiyan, C. Muthukrishnan, and R. Murugesan, J. Mol. Struct. **648**, 1 (2003).
[37] T. F. Yen, L. J. Boucher, and E. C. Tynan, Electron Spin Resonance of Metal Complexes, Plenum Press, New York 1969.
[38] F. Düzgün and B. Karabulut, J. Mol. Struct. **834**, 136 (2007)
[39] U. B. Gangadhamath, S. M. Annigeri, A. D. Naik, V. K. Revankar, and V. B. Mahale, Mol. Struct. (Theochem), **572** 61 (2001).
[40] R. Bıyık and R. Tapramaz, Z. Naturfosch. **61a**, 171 (2006).