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Characterizing the paramagnetic behavior of Cu^{2+} doped nickel(II) dipicolinato by using theoretical and experimental EPR and UV–vis studies

İlkay Yıldırım [a], Yunus Çelik [b], Bünyamin Karabulut [c,*]

[a] Department of Radiotherapy, Vocational School of Health Services, Biruni University, Topkapı, 34010 Istanbul, Turkey
[b] Department of Physics, Faculty of Arts and Science, Ondokuz Mayıs University, Atakum, 55139 Samsun, Turkey
[c] Department of Computer Engineering, Faculty of Engineering, Ondokuz Mayıs University, Atakum, 55139 Samsun, Turkey

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ABSTRACT

In this study, the paramagnetism in bis(hydrogeno pyridine-2,6-dicarboxylato) nickel(II) trihydrate, $[Ni(Hdpc)_2]\cdot 3H_2O$, has been investigated after doping the sample with Cu^{2+} ions. The g and hyperfine parameters were obtained by electron paramagnetic resonance (EPR) experiments performed at ambient temperature. The study shows that Cu^{2+} ion defects the structure and exists interstitially in the lattice having a distorted local environment. It also shows the existence of two magnetically inequivalent Cu^{2+} sites. Experimental values for both EPR and optical spectrum studies were verified by using the appropriate theoretical approaches.

1. Introduction

Transition metal ions are widely used as dopants to form paramagnetic centers [1–3]. Electron Paramagnetic Resonance (EPR) technique is used to characterize the spin dynamics and local symmetries of such centers [4–6]. Copper (II) ion has $3d^9$ electron configuration and so can be thought as having a simple magnetic hole system. It is commonly preferred as dopant and gives detailed information about the ground state and the local symmetry of the center [7–9]. The doped Cu^{2+} ion can either replace the tri-, di-, and monovalent ions, settle interstitially in diamagnetic host crystals or forms its own local structure [10–12].

The water-soluble pyridine-2,6-dicarboxylic acid (dipicolinic acid; H_2dpc) has great biological functions. It is used as an enzyme inhibitor, plant preservative and food cleaner [13–21]. From structural point of view, it is a versatile ligand which displays a variety of coordination modes with its neutral form (H_2dpc), anionic univalent ($Hdpc^-$) and divalent (dpc^{2-}) forms [22]. However, it is generally tridentate ligand chelating through N,O,O donor sites.

2. Experimental

Ethanol solution of pyridine-2,6-dicarboxylic acid (0.225 g, 1.35 mmol) and $NiCl_2\cdot 6H_2O$ (0.032 g, 0.135 mmol) were rigorously stirred for ten minutes at ambient temperature. After two weeks, green-colored single crystals of the complex were isolated from the solution. To dope $[Ni(Hdpc)_2]\cdot 3H_2O$ complex with Cu^{2+} impurities, small amount of $CuCl_2\cdot 2H_2O$ (0.05% by wt) was added to saturated aqueous solution of $[Ni(Hdpc)_2]\cdot 3H_2O$ and left for slow evaporation at ambient temperature. Well-developed single crystals of Cu^{2+} doped sample were selected for EPR measurements.

X-ray structure determination studies on $[Ni(Hdpc)_2]\cdot 3H_2O$ single crystal show that the complex belongs to the monoclinic crystal system with space group $P2_1/c$. The unit cell parameters are given as: $a = 13.679(1)$Å, $b = 10.0450(9)$Å, $c = 13.767(2)$Å, $\beta = 115.184(7)^\circ$ and $Z = 4$ [22]. It was also reported that the coordination geometry around Ni(II) ion is an octahedron with two pyridine-2,6-dicarboxylic acids.

EPR spectra were recorded on a Varian E-109C X-band EPR spectrometer. Optical absorption spectra were recorded on a Scinco S-3100 PDA UV–vis spectrophotometer.

3. Results and discussion

3.1. Experimental studies

The a^*c, ba^* and cb planes were used to record the EPR spectra of Cu^{2+} doped $[Ni(Hdpc)_2]\cdot 3H_2O$ single crystal at room temperature. One of the EPR spectra of the complex in ba^* plane is given in Fig. 1. The spectrum has five wide peaks and three tiny shoulders giving a total of eight peaks. It indicates the hyperfine

* Corresponding author.
E-mail address: bbulut@omu.edu.tr (B. Karabulut).

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splitting (A) because of the nuclear spin ($I = 3/2$) of at least two Cu^{2+} ions. To distinguish whether they form two distant centers or sites in the host lattice, the angular variations of both g^2 and A^2 should be plotted. The graph is shown in Fig. 2 and it clearly indicates the anisotropy and site symmetry of two Cu^{2+} ions. There are two magnetic inequivalent sites in ba^* and cb planes. The sites coincide or feel the same external magnetic field as the crystal being rotated in a^*c plane in the host lattice. This behavior of the EPR spectra corresponds to a paramagnetic sample with monoclinic crystal system. Noting also that since the ionic radius of Ni^{2+} (69 pm) is smaller than that of Cu^{2+} (72 pm), Cu^{2+} ions are said to be located interstitially and arranged its environment in the lattice.

The principal values of **g** and **A** tensors for Cu^{2+} doped $[Ni(Hdpc)_2]\cdot 3H_2O$ complex were calculated by considering the rhombic spin Hamiltonian (SH) [23]:

$$H = \beta\left(g_xB_xS_x+g_yB_yS_y+g_zB_zS_z\right)+A_xI_xS_x+A_yI_yS_y+A_zI_zS_z \quad (1)$$

The Hamiltonian includes only electron Zeeman and hyperfine interactions. The principal values of **g** and **A** tensors can be evaluated by the fitting procedure defined in Ref [24]. The calculated SH parameters (g and A values) are given in Table 1. Results indicate that a rhombic distortion exist for the Cu^{2+} ions in $[Ni(Hdpc)_2]\cdot 3H_2O$ complex. In rhombic distortion, the unpaired electron of the Cu^{2+} ion spends its time in either $d_{x^2-y^2}$ or $d_{3z^2-r^2}$ orbitals. The ground state wave functions of two copper(II) sites can be calculated using SH parameters as follows:

$$\psi_I = 0.83\left|d_{x^2-y^2}\right\rangle+0.56\left|d_{3z^2-r^2}\right\rangle$$

$$\psi_{II} = 0.98\left|d_{x^2-y^2}\right\rangle+0.19\left|d_{3z^2-r^2}\right\rangle$$

There are two main bands in the optical absorption spectrum of Cu^{2+} doped $[Ni(Hdpc)_2]\cdot 3H_2O$ complex occurring at 15674 and 19194 cm^{-1}, respectively. The first band is assigned to E_{xy} ($d_{x^2-y^2}\leftrightarrow d_{xy}$ transition) and the second band is assigned to $E_{xz}=E_{yz}$ ($d_{x^2-y^2}\leftrightarrow d_{xz}$, d_{yz} transition) energies of Cu^{2+} ion in a distorted octahedral site. Neglecting overlap integrals and small terms, the general expressions for the molecular orbital (MO) bonding parameters related to SH and optical absorption values [25] are given as follows:

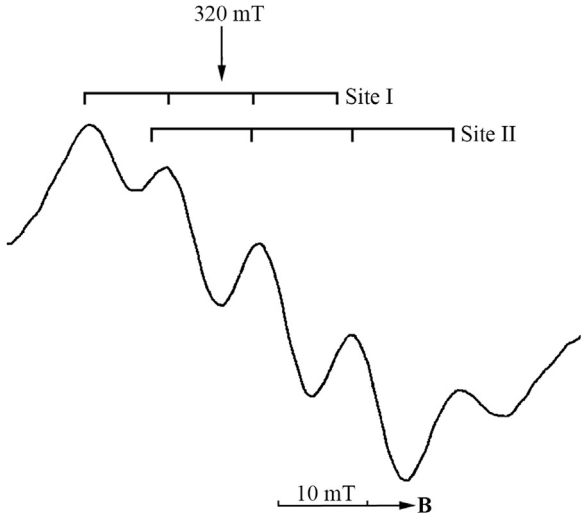

Fig. 1. EPR spectra of Cu^{2+} doped $[Ni(Hdpc)_2]\cdot 3H_2O$ single crystal when the magnetic field in the ba^* plane 30° away from the b-axis.

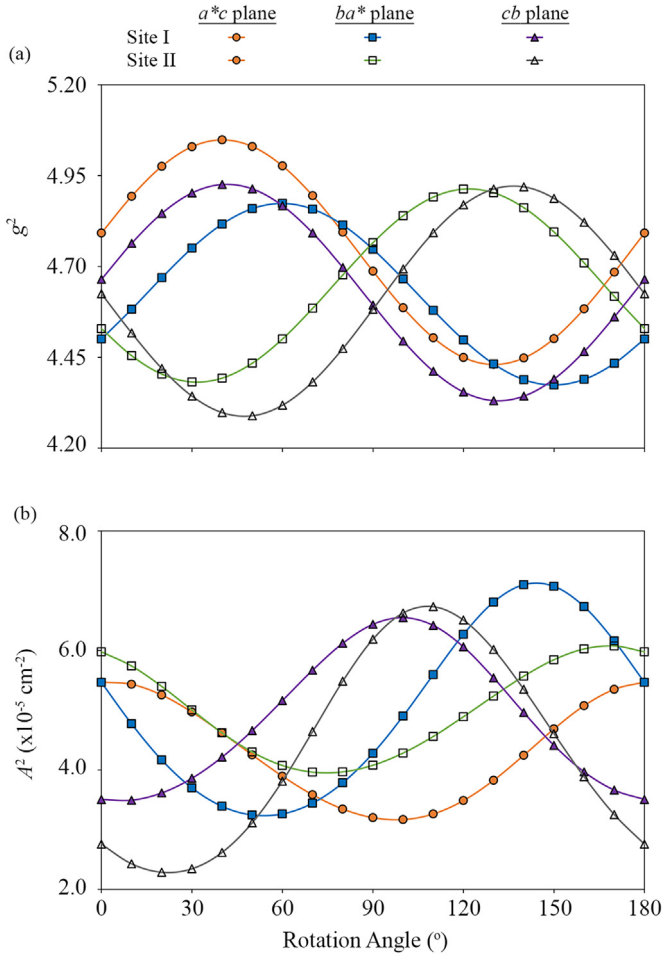

Fig. 2. Angular variations of (a) g^2 and (b) A^2 values of the EPR spectra in all planes for Cu^{2+} doped $[Ni(Hdpc)_2]\cdot 3H_2O$ single crystal.

$$g_z = g_e-\frac{8\alpha_0^2\beta_1^2\zeta_0}{E_{xy}} \quad (2a)$$

$$g_y = g_e-\frac{2\alpha_0^2\beta_0^2\zeta_0}{E_{xz}} \quad (2b)$$

$$g_x = g_e-\frac{2\alpha_0^2\beta'^2\zeta_0}{E_{yz}} \quad (2c)$$

$$\alpha_0^2 = \frac{7}{12}\left[\left(\frac{A_x+A_y-2A_z}{P_0}\right)+2\Delta g_z-\left(\frac{5}{14}\right)\left(\Delta g_x+\Delta g_y\right)\right] \quad (3)$$

$$\kappa = \frac{1}{\alpha_0^2}\left[-\frac{A_z}{P_0}-\left(\frac{4}{7}\right)\alpha_0^2+\Delta g_z+\left(\frac{3}{14}\right)\left(\Delta g_x+\Delta g_y\right)\right] \quad (4)$$

where $g_e\approx 2.0023$ is the free electron g factor, ζ_0 and P are the spin orbit coupling parameter and dipolar hyperfine structure constant, respectively, for free Cu^{2+} ion ($\zeta_0\approx 829 cm^{-1}$ [26], $P_0\approx 388\times 10^{-4} cm^{-1}$ [27]). κ is the core polarization constant, α_0^2, β_1^2, β_0^2, β'^2 are the MO bonding coefficients for the central ion. The results and comparison to the other Cu^{2+} ion containing lattices are given in Table 2. The value of α_0^2 indicates the nature of σ