Quadrupole Effects in ^{14}N and ^{2}D Ligand ENDOR Studies of a Bis(glycinato)-Cu(II) Complex in Triglycine Sulfate Single Crystals

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The analysis of the ^{14}N and ^{2}D quadrupole interactions in the bis(glycinato)-Cu(II) complex in triglycine sulfate single crystals reveals the efficiency of the ENDOR method. In both cases the complete quadrupole tensors are measured and analyzed. The ^{14}N quadrupole couplings are explained using the Townes-Dailey approach to obtain the electronic population near the nitrogens. Using the well known relationship between the ^{2}D couplings and the N–D bond lengths as well as the fact that the axis corresponding to the tensor component of largest magnitude lies along the N–D bond, the position of the deuterons in this Cu(II) complex is estimated.

1. Introduction

Nuclear quadrupole couplings can be determined by EPR, NMR, NQR, microwave and Mössbauer spectroscopy. For paramagnetic ions and free radicals in magnetically diluted solids, electron-nuclear double-resonance (ENDOR) can also be used. The analysis of ENDOR spectra is more complicated than that of NMR and NQR spectra. The unpaired electrons produce a local magnetic field B_{loc} depending on the hyperfine interaction and the electron spin quantum number M_s. The nuclear spins are quantized along the effective field, which is the vector sum of the external field B and the local field B_{loc}. If the energy of the ^{2}D and ^{14}N nuclear spins in the effective field is larger than the quadrupole interaction energy, each of its ENDOR lines is split into 2 lines of equal intensities. The doublet splitting depending on the electron spin quantum number M_s permits one to determine accurately all elements of the quadrupole coupling tensor [1].

The detection of ENDOR signals is only possible if the NMR and EPR transitions of the center under consideration are at least partially saturatable. Usually for transition metal complexes at room temperature the spin-lattice relaxation times are rather short and the detection of ENDOR signals is possible only below 30 K.

The higher sensitivity of ENDOR compared to NMR and NQR is due to the fact that the spin temperature of the nuclear pool is effectively coupled to that of the paramagnetic electron pool. Therefore, strong ENDOR signals are obtained if the magnetic hyperfine coupling A is larger compared to the nuclear Zeeman energy $g_N \beta_N B$. ENDOR investigations need single crystals of a few cubic millimeter, the investigation of powder samples is possible.

The quadrupole tensor elements are usually obtained from the angular dependence of the readily observable first order splitting $\Delta \nu_Q$.

2. ^{14}N and ^{2}D Quadrupole Effects on the Cu(II)-bisglycinato-complex

EPR and ENDOR spectra of Cu(II) ions in α-glycine, *l*-alanine and ferroelectric triglycine sulfate (TGS) single crystals performed by several authors [2–4] reveal that in all crystals the Cu(II) ions form a planar Cu(II) complex with two nitrogens. Ligand ENDOR spectra of this complex in TGS crystals reveal the point symmetry C_1, i.e. all ligand nuclei are magnetically inequivalent [5].

The analysis of the ^{14}N and ^{2}D ENDOR spectra of these complexes yields the complete electron-nuclear magnetic dipole and electric quadrupole hyperfine interaction tensors. The ^{14}N quadrupole couplings are a sensitive indicator of the total elec-

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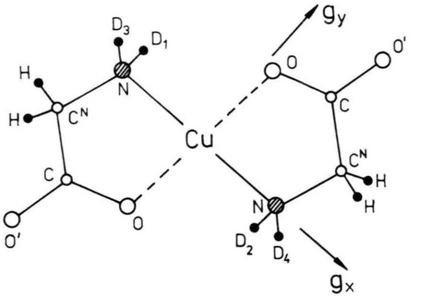

Fig. 1. Model of the Cu(II)-bisglycinato complex.

tronic distribution around nitrogen whereas the ^{2}D quadrupole couplings give the bond lengths and angles of the deuterons which enables one to estimate their position in the Cu(gly)$_2$complex.

The ENDOR spectra were analyzed with the following standard spin Hamiltonian:

$$\hat{H}_s = \beta \boldsymbol{B} \cdot \tilde{g} \cdot \hat{\boldsymbol{S}} + \hat{\boldsymbol{S}} \cdot \tilde{A}^{\mathrm{Cu}} \cdot \hat{\boldsymbol{I}}^{\mathrm{Cu}} + \hat{\boldsymbol{I}}^{\mathrm{Cu}} \cdot \tilde{Q}^{\mathrm{Cu}} \cdot \boldsymbol{I}^{\mathrm{Cu}}$$
$$+ \sum_{i=1}^{2} (\hat{\boldsymbol{S}} \cdot \tilde{A}^{\mathrm{N_i}} \cdot \hat{\boldsymbol{I}}^{\mathrm{N_i}} + \hat{\boldsymbol{I}}^{\mathrm{N_i}} \cdot \tilde{Q}^{\mathrm{N_i}} \cdot \hat{\boldsymbol{I}}^{\mathrm{N_i}} - \beta_{\mathrm{N}} g_{\mathrm{N}} \boldsymbol{B} \cdot \hat{\boldsymbol{I}}^{\mathrm{N_i}})$$
$$+ \sum_{j=1}^{4} (\hat{\boldsymbol{S}} \cdot \tilde{A}^{\mathrm{D_j}} \cdot \hat{\boldsymbol{I}}^{\mathrm{D_j}} + \hat{\boldsymbol{I}}^{\mathrm{D_j}} \cdot \tilde{Q}^{\mathrm{D_j}} \cdot \hat{\boldsymbol{I}}^{\mathrm{D_j}} - \beta_{\mathrm{N}} g_{\mathrm{D}} \boldsymbol{B} \cdot \hat{\boldsymbol{I}}^{\mathrm{D_j}}) .$$

The differences of the principal values of the quadrupole tensors $Q^{\mathrm{N_1}}$ and $Q^{\mathrm{N_2}}$ as well as $Q^{\mathrm{D_1}}(Q^{\mathrm{D_2}})$ and $Q^{\mathrm{D_3}}(Q^{\mathrm{D_4}})$ are of the same order of magnitude as the experimental error. Therefore averaged tensor elements are used for the analysis.

2.1. ^{14}N *ENDOR Spectra of TGS*:Cu^{2+}

The ^{14}N ENDOR spectra of the Cu(gly)$_2$ complex consist of four groups of lines which for the static magnetic field perpendicular to the $a \cdot \sin\beta$-axis show a doublet splitting with equal intensities. This doublet splitting is due to the magnetic nonequivalency of the ^{14}N nuclei.

The following tensor elements (in MHz) given in coordinate system x', y', z' are used for the electron population analysis proposed by Townes and Dailey [6].

$$Q = \begin{pmatrix} 0.822 & -0.290 & 0.287 \\ -0.290 & 0.298 & -0.187 \\ 0.287 & -0.187 & -1.120 \end{pmatrix}.$$

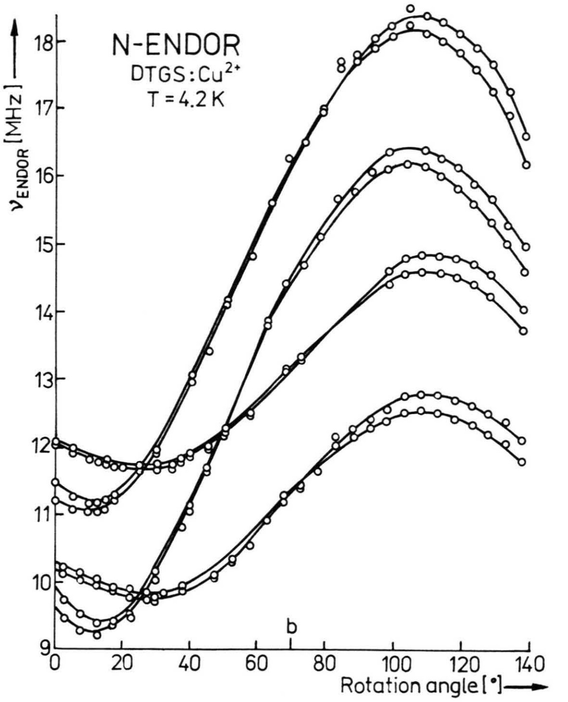

Fig. 2. Angular dependence of ^{14}N ENDOR lines, rotation axis a sin β.

For the construction of the hybridized orbitals we used a nonplanar geometry around the ligand nitrogen coordinated to the Cu(II) ion. The bond angles and distances are taken from X-ray data of the undoped TGS lattice and from EPR investigations and molecular orbital calculations on this complex [7, 8].

The populations of the hybridized orbitals as found are

$$n_{\mathrm{Cu}} = 1.82 , \quad n_{\mathrm{C}} = 1.45 , \quad n_{\mathrm{H_1}} = 1.39 , \quad n_{\mathrm{H_2}} = 1.60 ,$$

and the total nitrogen atom L-shell population $N_{\mathrm{T}} = 6.26$ is obtained. The s/p ratio of the Cu orbital is rather sensitive to a change of the position of the plane spanned by H$-$N$-$H. Its numerical values is in agreement with that obtained from the magnetic nitrogen hyperfine splitting [1].

2.2. ^{2}D *ENDOR spectra of TGS*:Cu^{2+}

The ^{2}D ENDOR spectra of the Cu(gly)$_2$ complex consist of 16 lines which may be divided into 2 groups. Within the groups the deuterons have

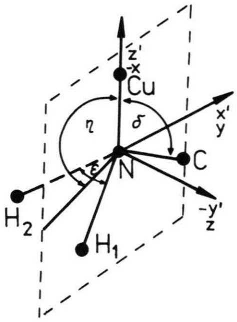

Fig. 3. Geometry of bonds surrounding nitrogen.

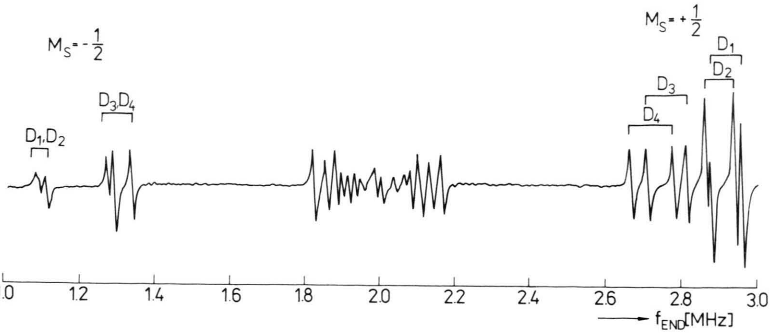

Fig. 4. ^{2}D ENDOR spectrum.

about the same coupling constants and asymmetry parameters:

$$\left(\frac{e^2 q\, Q}{h}\right)_{D_1,\, D_2} = 188\ \text{kHz}\,, \quad \left(\frac{e^2 q\, Q}{h}\right)_{D_3,\, D_4} = 180\ \text{kHz}\,,$$

$$\eta_{D_1,\, D_2} = 0.18\,, \quad \eta_{D_3,\, D_4} = 0.09\,.$$

Reuveni [9] found the empirical relation

$$\frac{e^2 q\, Q}{h}\,[\text{kHz}] = -273 + \frac{432}{R^3[\text{Å}]}$$

between the ^{2}D quadrupole coupling parameter and the N–H bond lengths. This formula can reproduce the N–H distance to within ±0.006 Å. We estimated the bond lengths $R_{1,2} = 1.022$ Å and $R_{3,4} = 1.016$ Å in the amino groups. Assuming the principle axis of the quadrupole tensor to be almost parallel to the N–D direction we calculated the D–N–D angle in the amino groups and obtained $\varphi = 108.9°$. This leads also to the conclusion that during the formation of the bisglycinato-Cu(II) complex when one deuteron of each ND$_3$ group is removed the remaining deuterons were reoriented by a rotation of the ND$_2$ groups about the g_y axis by an angle of 30°.

Under the assumption of C_i symmetry and using the bond lengths Cu–N 2.00 Å, Cu–O 1.95 Å the distances of the deuterons D^{1,2} and D^{3,4} from Cu amount to 2.32 Å and 2.72 Å, respectively.

3. Conclusion

Until now in publications on the analysis of the electronic structure and the position of ligand nuclei in transition metal complexes using ENDOR spectroscopy the analysis of the magnetic interactions dominates. Analyses of the quadrupole couplings are rather scarce.

The ^{14}N nuclei quadrupole couplings are a sensitive indicator of the total electronic distribution around a nitrogen nucleus, whereas the magnetic nuclear hyperfine couplings depended only on the unpaired spin distribution. The empirical formulae for the interpretation of the ^{2}D nuclear quadrupole couplings enable one to determine the exact position of the nuclei whereas an analysis of the magnetic interactions reveals exact positions only for nuclear distances $\geqq 2$ Å when the classical point-dipole interaction model may be applied.

For the here discussed examples $\hat{H}_Q \ll (\hat{H}_{IS} + \hat{H}_{IB})$ holds and the analysis of their ENDOR spectra is routine work. But the recently detected ^{14}N ENDOR of a Cu(II)-bis(diethyl-dithiocarbamate) complex [10] points to a dominating quadrupole interaction. This is confirmed by a calculation of the angular dependence of line positions and line intensities using the formalism of Muha [11]. In case of $A \approx 2\, g_N \beta_N B$ the frequencies of the transition with $AM_s > 0$ show the same behaviour as known from the NQR spectra in case of Zeeman perturbation: the resonance lines are almost constant in the rotation pattern but their intensities are strongly angular dependent.

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