

EPR AND SPECTRAL STUDIES OF A MOLECULAR AND CRYSTAL STRUCTURE OF $\text{Cu}(3,5\text{-dimethylpyridine})_3(\text{NO}_3)_2$

S.K. HOFFMANN^a, M.A.S. GOHER^b, W. HILCZER^a, J. GOSLAR^a
AND A.K. HAFEZ^b

^a Institute of Molecular Physics, Polish Academy of Sciences
Smoluchowskiego 17/19, 60-179 Poznań, Poland

^b University of Alexandria, Department of Chemistry
Alexandria 21321-Ibrahimia, Egypt

(Received October 22, 1993)

X-band single crystal EPR, IR and UV-VIS data are used to deduce a molecular and crystal structure of a new compound with a chemical formula $\text{Cu}(3,5\text{-dimethylpyridine})_3(\text{NO}_3)_2$. EPR shows that four magnetically inequivalent molecules exist in the crystal unit cell of C_{4v} symmetry. IR spectra suggested that both monodentate and bidentate NO_3 -groups exist in the crystal. A most probable Cu(II) complex geometry with $d_{x^2-y^2}$ ground state is a square pyramid with three nitrogens from 3,5-dimethylpyridine molecules and one oxygen from monodentate nitrate group in a basal plane and an oxygen from NO_3 -group in apical position. There exists a chemical contact between complexes as it is indicated by the exchange interaction with $|J| \leq 1 \text{ cm}^{-1}$. It suggests that square pyramid complexes are arranged in polymeric chains with semi-coordination of bidentate NO_3 -group to the adjacent Cu(II) ion. An extended analysis of an exchange averaging effect between EPR lines from two and four Cu(II) sites is presented with equations relating molecular and crystal g -factors.

PACS numbers: 33.20.Ea, 61.66.-f, 76.30.Da

1. Introduction

Materials for EPR studies are available in most cases in a powder or polycrystalline form. In such cases EPR spectrum gives spatially averaged EPR information and an interpretation is needed to extract values of EPR parameters. It is relatively easy to do for magnetically diluted systems, as paramagnetic ion doped diamagnetic crystal or free radical centers produced by ionizing radiation, especially with a computer simulation technique. In condensed paramagnets, however, where a dominant role play exchange and dipolar interactions between paramagnetic centers a situation is more complicated mainly due to an exchange averaging

effect. We will discuss this for Cu(II) compound with a single unpaired electron ($S = 1/2$) per ion.

At least three problems appear in an interpretation of powder EPR spectra in condensed paramagnets: (1) Is it possible to determine uniquely the true values of EPR parameters from a powder spectrum? The true values mean the values determined from single crystal EPR measurements; (2) Is it possible to conclude from the crystal EPR parameters about molecular parameters of an individual non-coupled paramagnetic center and its electronic ground state wave function? (3) Can EPR give some indications about molecular and crystal structure of a compound when these data are not available?

In principle an answer for these questions is positive but only for simple cases and generally circumspection is recommended. In our recent papers [1–3] we have stressed that EPR parameters determined from powder Cu(II) spectra can differ markedly from those determined from angular measurements in single crystals even when computer simulations are performed. It is because of a line width and line shape angular dependence is very often not predictable [3] and moreover some “false” additional peaks can appear in the spectra of weakly coupled complexes [2–4].

We have found an unusual confusing powder EPR spectrum in Cu(3,5-dimethylpyridine)₃(NO₃)₂ which crystal structure is unknown. A typical interpretation of the powder spectrum is in a contradiction to single crystal EPR data. Moreover an axial symmetry of g^2 -tensor was found what is a very rare case in crystals with magnetically inequivalent Cu(II) complexes.

In this paper detailed studies on Cu(3,5-dimethylpyridine)₃(NO₃)₂ are reported and a discussion of exchange averaging of four EPR lines from four inequivalent sites in a crystal is presented. On this basis with a support from spectroscopic IR and UV-VIS data some conclusions on molecular and crystal structure of the compounds are drawn.

2. Experimental

2.1. Preparation

Cu(NO₃)₂ · 3H₂O (0.97 g, 4 mmol) dissolved in ethanol was mixed with 3,5-dimethylpyridine (2.14 g, 20 mmol). To this mixture an aqueous solution of NaN₃ (0.26 g, 4 mmol) was added dropwisely, and the mixture shaken after each addition until deep green colored solution was obtained. This mixture was allowed to stand over several days to produce black and green crystals of the copper(II) azide complexes. These crystals were filtered and the filtrate allowed one again to stand over several days until quartz blue well developed crystals of the title complex separated. Elemental analysis results (% , with calculated values in parenthesis) found for CuC₂₁H₂₇N₅O₆: Cu 12.14 (12.48), C 49.92 (49.56), H 5.55 (5.35), N 13.42 (13.75).

2.2. Spectral measurements

UV-VIS spectra of a solid muller in Nujol were measured on a ZEISS-JENA VSU-1 spectrophotometer with MgO as a standard. Infrared spectra were recorded

in the region of 200–400 cm^{-1} with a UNICAM SP-2000 instrument on solid complex in a Nujol mull.

2.3. EPR measurements

EPR spectra were recorded on a X-band RADIOPAN SE/X-2547 spectrometer with a cylindrical cavity TM_{110} and 100 kHz magnetic modulation equipped with flowing helium OXFORD ESR-900 cryostat. Single crystal EPR spectrum angular dependence was measured by rotation of a crystal in the microwave cavity in 10 degree interval. The dependence was measured in 1,2,3 orthogonal reference system referred to the crystal habit (see inset of Fig. 3) with 3-axis being perpendicular to the largest crystal plane.

3. Results

3.1. Electronic and infrared spectra

Our interest in the infrared spectrum of the title complex lies mainly in the absorption bands related to nitrate groups, since 3,5-dimethylpyridine acts as a monodentate ligand. The spectrum of the solid complex shows the following absorption bands (cm^{-1} , ν — very strong, s — strong, m — medium, sh — shoulder): 1470 sh,s , 1430 s , 1380 vs , 1310 s and 1280 ms . These bands are indicative of the existence of mono- and bidentate nitrate groups in the complex [5, 6]. In fact these absorption bands are very similar to corresponding bands reported for $[\text{Cu}(\text{NO}_3)_2(\text{N}_3)_2(3\text{-picoline})_4(\text{H}_2\text{O})]$ complex containing both monodentate and bridging bidentate nitrate groups as established by its X-ray crystal structure analysis [7]. The 1470 and 1280 cm^{-1} bands may be assigned to the N–O stretch of the bidentate nitrate group, whereas the other bands are related to the monodentate one.

The electronic spectrum (Fig. 1) of $\text{Cu}(3,5\text{-dimethylpyridine})_3(\text{NO}_3)_2$ measured as a solid mull in Nujol shows the $d-d$ absorption as an asymmetric band centered around 17240 cm^{-1} . The position of this ligand field band is consistent with tetragonal octahedral geometry around the copper atoms [8, 9].

3.2. EPR results

Powder EPR spectra recorded at 295 and 77 K are presented in Fig. 2. These spectra show that EPR parameters are temperature independent except a small line narrowing at low temperature. At first sight the powder spectra suggest axial crystal field symmetry with $g_{\parallel} > g_{\perp}$. However single crystal rotational data presented in Fig. 3 clearly indicate quite opposite g -factor sequence. Single crystal EPR spectrum consists of a single resonance line in all crystal orientations. The shape of the line is not exactly Lorentzian as expected for strongly exchange coupled systems but is over-Lorentzian (with higher wings) for the broadest lines in perpendicular orientations and under-Lorentzian (with a deviation towards the Gaussian shape) for the orientations with the narrowest line. It clearly indicates that the exchange interaction is not very strong in the crystal and only slightly overdominates the copper(II) hyperfine coupling. A confirmation of this is a large

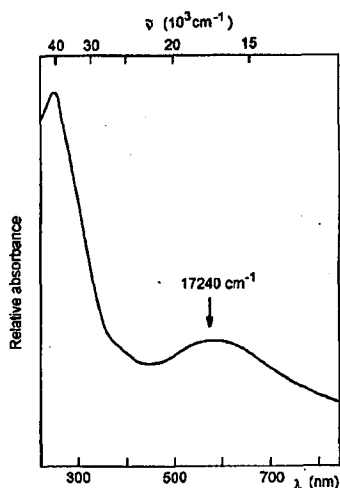


Fig. 1. UV-VIS spectrum of solid complex $\text{Cu}(3,5\text{-dimethylpyridine})_3(\text{NO}_3)_2$.

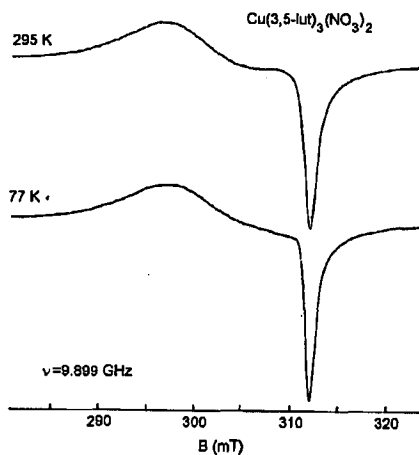


Fig. 2. Powder spectra of $\text{Cu}(3,5\text{-dimethylpyridine})_3(\text{NO}_3)_2$ recorded at 295 and 77 K.

anisotropy of the peak-to-peak line width value ΔB_{pp} ranging from 0.8 mT to 9.0 mT with extrema coinciding with the extrema in $B(\theta)$ dependence. Thus an exchange integral can be evaluated as $|J| \leq 1 \text{ cm}^{-1}$.

The $B(\theta)$ experimental plots (points in Fig. 3) indicate an axial g^2 -tensor symmetry with the symmetry axis "z" in the 2,3-plane along the direction with maximal B -value ($\theta \approx 45^\circ$). It is confirmed by g^2 -tensor calculations with a fitting of the experimental data to the equation

$$g^2(\theta) = \alpha + \beta \cos 2\theta + \gamma \sin 2\theta$$

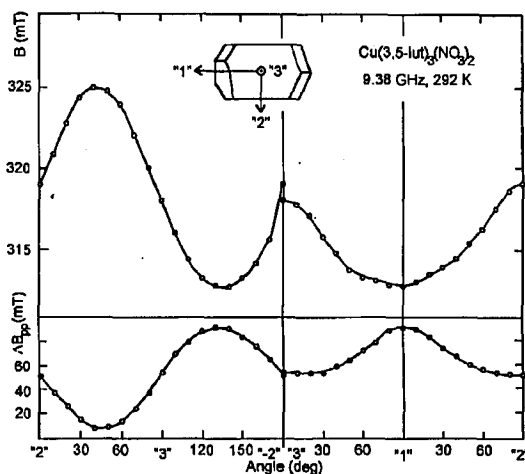


Fig. 3. Angular variations of the resonance field B and line width ΔB_{pp} in 1, 2, 3 reference frame related to the crystal habit (see inset). Solid lines are theoretical plots with parameters from Table.

in the three orthogonal planes. After a starting angle correction and g^2 -tensor component calculations the diagonalization gave principal crystal g -factors: $g_{\parallel} = 2.060$, $g_{\perp} = 2.147$. Although the g -factor values evaluated from the powder spectra are the same as in the crystal spectra, the $g_{\parallel} < g_{\perp}$ obtained from crystal data is in a contradiction to the powder spectrum suggestion. This discrepancy is clearly due to a large line width anisotropy with a more than ten times broader line in perpendicular g^2 -tensor orientations which leads to a confusing powder spectrum.

The line width angular dependence can be very well approximated by the equation

$$\Delta B_{pp} = \Delta B_{\parallel} \cos^2 \theta + \Delta B_{\perp} \sin^2 \theta,$$

where θ -angle is measured from the z -axis and parameters are summarized in Table. This type of $\Delta B_{pp}(\theta)$ behavior we have suggested recently as a typical for Cu(II) compounds [3] when dominant contribution arises from the hyperfine second moment.

A relatively low value of the g_{\perp} suggests that this is not a molecular g -factor describing an individual Cu(II) complex but it is rather an averaged g -factor from exchange coupled Cu(II) complexes with misaligned local crystal field symmetry axes. To obtain information about molecular parameters we have recorded EPR spectra of solutions of Cu(3,5-dimethylpyridine)₃(NO₃)₂ in chloroform, methanol and acetone. Liquid solutions spectra at 292 K and frozen solution (77 K) spectra are shown in Fig. 4 and EPR parameters are summarized in Table. The spectra and parameters are typical for Cu(II) coordinated by aromatic amines [10–12] with a relatively well resolved superhyperfine pattern from ¹⁴N atoms on the perpendicular peak. Number of the superhyperfine structure lines is 7 or 8. It can be explained as a result of interaction with three equivalent ¹⁴N nuclei leading to an intensity

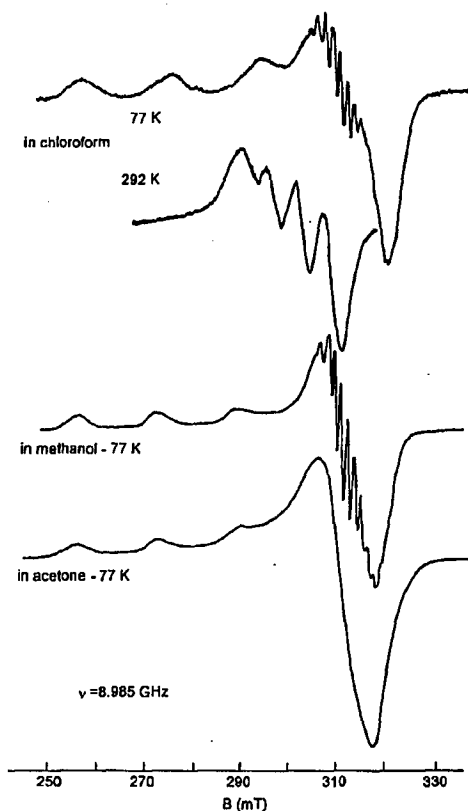


Fig. 4. Frozen solution (77 K) EPR spectrum and liquid solution spectrum of $\text{Cu}(\text{3,5-dimethylpyridine})_3(\text{NO}_3)_2$.

EPR parameters of $\text{Cu}(\text{3,5-dimethylpyridine})_3(\text{NO}_3)_2$. TABLE

Solid state crystal parameters:	$g_{\parallel} = 2.060(2)$, $g_{\perp} = 2.147(5)$ $\Delta B_{\text{pp}}^{\parallel} = 0.80(5)$ mT, $\Delta B_{\text{pp}}^{\perp} = 9.0(1)$ mT	
Evaluated molecular g -factors:	$g_z = 2.26(1)$, $g_y = 2.05(1)$, $g_x = 2.04(1)$	
Solutions:	Liquid	Frozen solution
in chloroform	$g_0 = 2.140(3)$ $a_0 = 59(2)$	$g_{\parallel} = 2.249(2)$, $g_{\perp} = 2.070(5)$ $A_{\parallel} = 196(3)$, $A_{\perp} \approx 0$, $A_N = 14(1)$
in acetone	$g_0 = 2.145(3)$ $a_0 = 62(2)$	$g_{\parallel} = 2.286(2)$, $g_{\perp} = 2.066(4)$ $A_{\parallel} = 178(3)$, $A_{\perp} \approx 10(3)$
in methanol	not detectable	$g_{\parallel} = 2.284(2)$ $A_{\parallel} = 178(3)$, $A_N = 13(1)$

Note: a_0 and A -values in 10^{-4} cm^{-1} .

ratio 1 : 3 : 6 : 7 : 6 : 3 : 1 and $A_{\perp}^{\text{Cu}} = 0$ or an interaction with three equivalent ^{14}N nuclei and $A_{\perp}^{\text{Cu}} = A_{\text{N}}$ leading to an intensity ratio 1 : 4 : 9 : 13 : 13 : 9 : 4 : 1, respectively. The first interpretation seems to be more probable since $A_{\perp} \approx 0$ is generally observed in Cu(II) complexes with aromatic amines. Both interpretations confirm a coordination of three equivalent 3,5-dimethylpyridine molecules and $d_{x^2-y^2}$ ground state. It must be kept in mind, however, that geometry of Cu(II) complex in solid state not necessarily must be the same as in solution where interionic couplings are negligible [10]. Also freezing can disturb the complex geometry as it is seen from a comparison between $g_0 = 2.140$ in chloroform liquid solution and $g_{\text{av}} = 2.129$ after freezing. Thus g_0 , g_{\parallel} and g_{\perp} of solutions give only approximate values expected in the crystal.

4. A relation between averaged crystal g -factors and local molecular g -factors

An exchange interaction between magnetically inequivalent paramagnetic centers leads to averaging of EPR lines. Instead of a set of the lines from differently oriented centers in a crystal unit cell one observes a single resonance line in an average position in magnetic field. In principle, if the local crystal field symmetry axes of the inequivalent sites are known from crystallographic data, one can calculate averaged crystal g -factors from molecular g -factors, or more precisely one can find crystal g^2 -tensor from local molecular g^2 -tensors. It is especially easy for two inequivalent sites [13, 14], i.e. for monoclinic crystals and when local g^2 -tensors have axial symmetry [15]. Below we will summarize results for two-center case and then we will introduce a new result for four-center case.

4.1. Two-center averaging

If the local x , y , z axes of a center with g_x , g_y , g_z principal g -values are oriented in a laboratory orthogonal reference frame as shown in Fig. 5 the principal g -factors g_a , g_b , g_c of the averaged crystal g^2 -tensor are for C_{2v} symmetry [14] ($\phi_1 = \phi_2 = \pi/2$) as follows:

$$g_a^2 = g_x^2,$$

$$g_b^2 = g_y^2 \sin^2 \beta + g_z^2 \cos^2 \beta, \quad (1)$$

$$g_c^2 = g_y^2 \cos^2 \beta + g_z^2 \sin^2 \beta$$

(when y -axes are parallel: $x \rightarrow y$, $y \rightarrow x$). For C_{2h} or C_2 symmetry ($\phi_1 = \phi_2$):

$$g_a^2 = (A - B)/2,$$

$$g_b^2 = g_y^2 \sin^2 \beta + g_z^2 \cos^2 \beta - (g_y^2 - g_x^2) \tan^2 \beta \cos^2 \phi, \quad (2)$$

$$g_c^2 = (A + B)/2,$$

where

$$A = g_x^2 + g_y^2 \cos^2 \beta + g_z^2 \sin^2 \beta + (g_y^2 - g_x^2) \tan^2 \beta \cos^2 \phi,$$

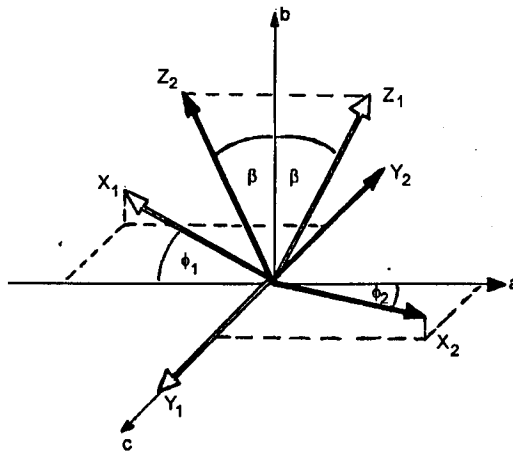


Fig. 5. Orientations of the local molecular g^2 -tensor axes x , y , z in the laboratory frame a , b , c . The b -axis is a twofold symmetry axis. The z -axes lie in ab -plane.

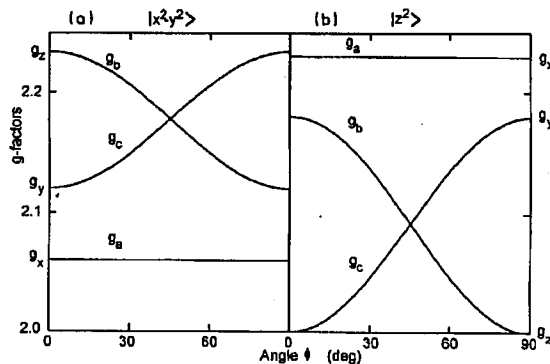


Fig. 6. Dependence of the crystal g -factors on the β -angle for: (a) $d_{x^2-y^2}$ ground state with molecular g -factors $g_x = 2.060$, $g_y = 2.120$, $g_z = 2.234$; (b) d_{z^2} ground state and $g_x = 2.230$, $g_y = 2.180$, $g_z = 2.000$.

$$B^2 = \left[-g_x^2 + g_y^2 \cos^2 \phi \pm g_z^2 \sin^2 \phi - \cos^2 \phi (2 + \tan^2 \phi) \right]^2 \\ + 4(g_y^2 - g_x^2)^2 \cos^2 \phi (1 - \cos^2 \phi / \cos^2 \phi).$$

The equations (1) and (2) are valid for both $d_{x^2-y^2}$ and d_{z^2} ground states of Cu(II) and a typical relationship between molecular and crystal g -factors in C_{2v} symmetry is presented in Fig. 6. As can be seen from Eq. (1) and Fig. 6 for a specific case an axial crystal g^2 -tensor appears. It is when local z -axes are mutually perpendicular ($\equiv \pi/4$) and then

$$g_{\parallel}^{\text{cryst}} = g_a = g_x,$$

$$g_{\perp}^{\text{cryst}} = [(g_x^2 + g_y^2)/2]^{1/2}$$

and a "reversed" crystal g^2 -tensor and EPR powder spectrum are observed with $g_{\parallel} < g_{\perp}$ for $d_{x^2-y^2}$ and $g_{\parallel} > g_{\perp} = 2.0$ for d_{z^2} .

4.2. Four-center averaging

General expressions for averaged g -factors of four paramagnetic centers are not available although such a situation commonly appears in orthorhombic and tetragonal crystals. In our recent papers [1, 16] we proposed decoupling procedures for such cases which can be used when at least at some crystal orientations, the lines from inequivalent sites are partially resolved in a single crystal EPR spectrum. Below we will derive the equations for $Z = 4$ in C_{4v} and C_{2v} symmetry and we will look for cases when the averaged spectrum has an axial symmetry as we observed in a $\text{Cu}(3,5\text{-dimethylpyridine})_3(\text{NO}_3)_2$ crystal.

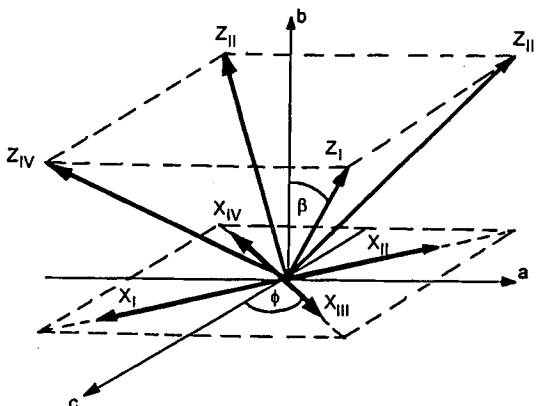


Fig. 7. Orientation of the local g^2 -tensor axes (only x and z are shown) for four magnetically inequivalent centers. The x -axes lie in ac -plane.

A geometry of the problem is shown in Fig. 7. Orientations of the local x , y , z axes in a , b , c reference frame is given by the direction cosines matrix

$$\begin{pmatrix} \sin \phi & 0 & \cos \phi \\ \cos \phi \cos \beta & \sin \beta & \sin \phi \cos \beta \\ \cos \phi \sin \beta & \cos \beta & \sin \phi \sin \beta \end{pmatrix}$$

with β and ϕ angles defined in Fig. 7 and following signs of the cosines for the four centers:

	I	II	III	IV
x	$\begin{pmatrix} - & 0 & + \end{pmatrix}$	$\begin{pmatrix} + & 0 & - \end{pmatrix}$	$\begin{pmatrix} + & 0 & + \end{pmatrix}$	$\begin{pmatrix} - & 0 & - \end{pmatrix}$
y	$\begin{pmatrix} + & - & + \end{pmatrix}$	$\begin{pmatrix} - & - & - \end{pmatrix}$	$\begin{pmatrix} + & - & - \end{pmatrix}$	$\begin{pmatrix} - & - & + \end{pmatrix}$
z	$\begin{pmatrix} + & + & + \end{pmatrix}$	$\begin{pmatrix} - & + & - \end{pmatrix}$	$\begin{pmatrix} + & + & - \end{pmatrix}$	$\begin{pmatrix} - & + & + \end{pmatrix}$

Theoretical angular variations of the resonance field of I-IV centers with $d_{x^2-y^2}$ ground state of Cu(II) and local g -factors $g_x = 2.06$, $g_y = 2.120$, $g_z = 2.234$ for

$\beta = 20^\circ$ and $\phi = 25^\circ$ are shown in Fig. 8. The dashed lines in Fig. 8 show averaged g -factor angular dependence. The crystal g -factors are related to the local g -factors given by the equations

$$\begin{aligned} g_a^2 &= g_x^2 \sin^2 \phi + (g_y^2 \cos^2 \beta + g_z^2 \sin^2 \beta) \cos^2 \phi, \\ g_b^2 &= g_y^2 \sin^2 \beta + g_z^2 \cos^2 \beta, \\ g_c^2 &= g_y^2 \cos^2 \phi + (g_y^2 \cos^2 \beta + g_z^2 \sin^2 \beta) \sin^2 \phi. \end{aligned} \quad (3)$$

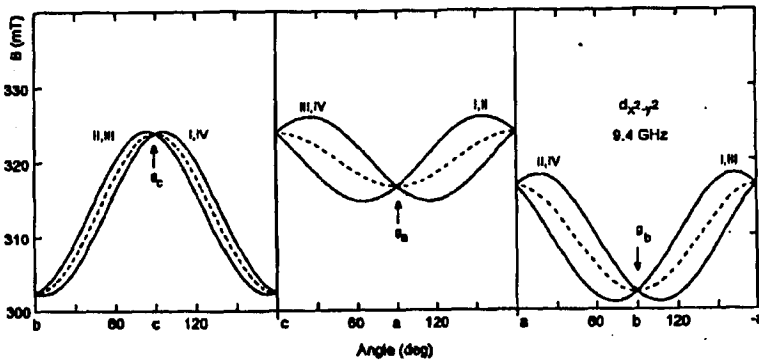


Fig. 8. Theoretical plot of angular variations of the resonance field for $Z = 4$ in a crystal unit cell with molecular g -factors: $g_x = 2.060$, $g_y = 2.120$, $g_z = 2.234$ (solid lines). Dashed lines show averaged plots with the crystal g -factors $g_a = 2.1207$, $g_b = 2.2210$ and $g_c = 2.0730$. The b -axis is a twofold symmetry axis and $\beta = 20^\circ$, $\phi = 25^\circ$, frequency 9.4 GHz.

Equations (3) show that the averaged g^2 -tensor is non-axial. However, in the case of C_{4v} symmetry ($\phi = 45^\circ$) an axial symmetry of the crystal g^2 -tensor appears with principal g -factors

$$\begin{aligned} (g_{\parallel}^{\text{cryst}})^2 &= g_y^2 \sin^2 \beta + g_z^2 \cos^2 \beta, \\ (g_{\perp}^{\text{cryst}})^2 &= (g_x^2 + g_y^2 \cos^2 \beta + g_z^2 \sin^2 \beta)/2. \end{aligned} \quad (4)$$

It is shown in Fig. 9, where angular variations of the local (solid lines) and averaged (dashed lines) resonance fields for $d_{x^2-y^2}$ and d_{z^2} ground states are presented.

It is clearly seen that an axial symmetry of the crystal g^2 -tensor appears when fourfold symmetry axis exists in our geometry independently whether the local g^2 -tensors are axial or non-axial both for $d_{x^2-y^2}$ and d_{z^2} states. Thus the general conclusion is that an observation of an axial crystal g^2 -tensor indicates C_{4v} symmetry of a crystal with $Z = 4$ or a special orientation of the local z -axes for $Z = 2$ in C_{2h} symmetry (z -axes are mutually perpendicular).

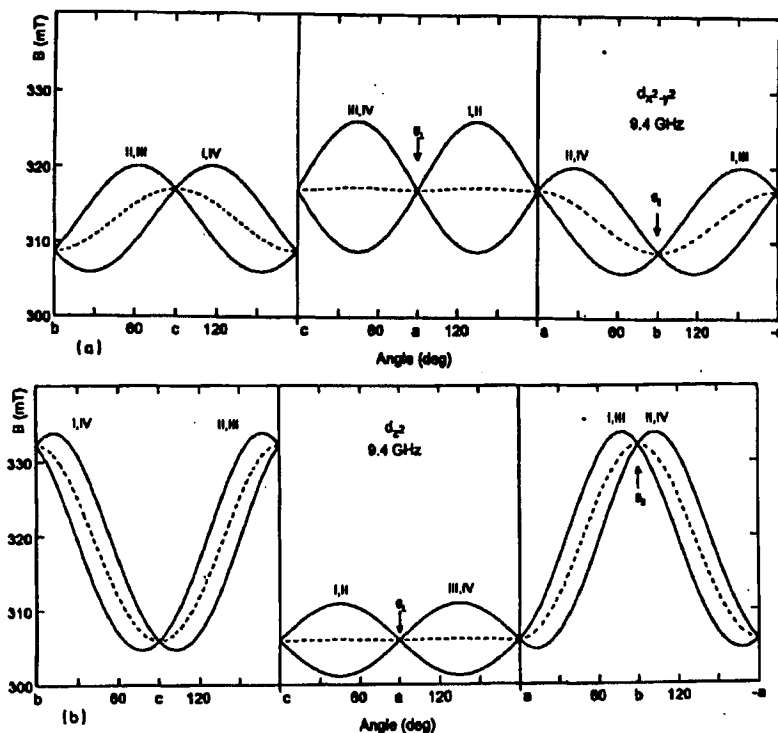


Fig. 9. Theoretical plots of angular variations of the resonance field for $Z = 4$ when b -axis is a fourfold symmetry axis; (a) for $d_{x^2-y^2}$ ground state with molecular g -factors $g_x = 2.060$, $g_y = 2.120$, $g_z = 2.234$, $\beta = 45^\circ$, $\phi = 45^\circ$, frequency 9.4 GHz (solid lines). Dashed lines represent averaged plots with the crystal g -factors $g_{\parallel} = 2.1778$, $g_{\perp} = 2.1197$; (b) for d_{z^2} ground state with $g_x = 2.230$, $g_y = 2.180$, $g_z = 2.000$, $\beta = 45^\circ$, $\phi = 45^\circ$, frequency 9.4 GHz (solid lines). Dashed lines represent averaged plots with the crystal g -factors $g_{\parallel} = 2.0219$, $g_{\perp} = 2.1952$.

5. Discussion

5.1. The ground state of Cu(II) and molecular g -factors

A crystal g^2 -tensor does not reflect local crystal field at Cu(II) sites but rather an overall crystal symmetry. Thus it does not contain information about the ground state wave function of copper(II) ions. We can conclude about the ground state from the other experimental facts.

Solution EPR data (see Table) suggest $d_{x^2-y^2}$ the ground state. Also the line width angular dependence governed by unresolved Cu(II) hyperfine structure indicates with no doubts that $d_{x^2-y^2}$ is the ground state. It is because maximal hyperfine splitting is expected along local z -axes both for $d_{x^2-y^2}$ and d_{z^2} states.

Thus for $d_{x^2-y^2}$ maximal line width value of the averaged EPR line is expected at the lowest resonance field as it is in $\text{Cu}(3,5\text{-dimethylpyridine})_3(\text{NO}_3)_2$ whereas the maximal ΔB_{pp} value for the d_{z^2} ground state should appear at the highest resonance field. Moreover, we have tried to fit rotational data of Fig. 3 with Eqs. (1-4) assuming the d_{z^2} ground state but without satisfactory results.

On the other hand the ground state not necessary should be a pure $d_{x^2-y^2}$ or d_{z^2} state. A mixing of these states in low symmetry complexes can appear with the resulting ground state

$$|0\rangle = a|d_{x^2-y^2}\rangle + b|d_{z^2}\rangle, \quad a^2 + b^2 = 1$$

as it has been found in $\text{Cu}(\text{py})_3(\text{NO}_3)_2$ [17] and in a Cu(II) doped $(\text{NH}_4)_2\text{SO}_4$ [18] crystal. In these cases, the a and b coefficients were temperature dependent due to the vibronic (pseudo Jahn-Teller) effect. In $\text{Cu}(3,5\text{-dimethylpyridine})_3(\text{NO}_3)_2$ however the g -factors are temperature independent thus we can assume a pure $d_{x^2-y^2}$ ground state of Cu(II) ions.

This assumption is confirmed by a computer fitting of the rotational data of Fig. 3. These data can be fitted with two models: assuming $Z = 2$ or $Z = 4$ in the crystal unit cell. For two inequivalent centers we have found satisfactory agreement for $g_{\parallel}^{\text{mol}} = 2.234$ and $g_{\perp}^{\text{mol}} = 2.06$ assuming that local z -axes are mutually perpendicular ($\beta = 45^\circ$ in Eq. (1)). However a better fit can be found assuming an existence of four molecules in the unit cell. It is a much more realistic assumption since rather a rhombic local crystal field is expected in the complex $\text{Cu}(3,5\text{-dimethylpyridine})_3(\text{NO}_3)_2$ since the $d_{x^2-y^2}$ ground state excludes trigonal bipyramid geometry (d_{z^2} state). Moreover the main crystal faces, i.e. 1,3-face and 1,2-face (see inset in Fig. 3) are mutually perpendicular suggesting an orthorhombic symmetry rather than monoclinic one. Another fact suggesting $Z = 4$ is that g_{\perp}^{cr} appears along axis 1 and in 2,3-plane at $\Theta = 45^\circ$. It is possible only when the angle between the crystal g^2 -tensor z -axis and 1-axis is also 45° . It clearly suggests that 1-axis is a fourfold symmetry axis of the crystal.

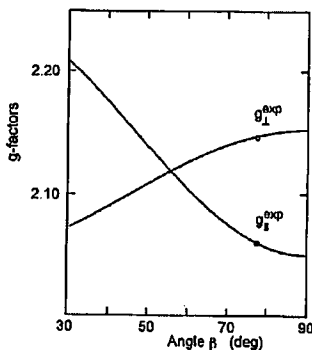


Fig. 10. Averaged crystal g -factors (g_{\parallel} and g_{\perp}) dependence on the β -angle between the local z -axes and fourfold symmetry axis for C_{4v} crystal symmetry assuming molecular g -factors $g_x = 2.04$, $g_y = 2.05$, $g_z = 2.26$. Experimentally determined crystal g -factors appear for $\beta = 78^\circ$.

Using Eq. (4) for $Z = 4$ one can try to find molecular g -factors g_x , g_y and g_z and β -angle. It cannot be done uniquely with such an accuracy as for the crystal g -factors but a good estimation can be made. We have made computer calculations for different sets of molecular g -factors taking into account two facts: $g_y \leq 2.06$ since $g_{\parallel}^{\text{cryst}}$ tends to g_y when β approaches 90° ; $g_x \leq g_y$ and the trace of the g^2 -tensor is the same for molecular and crystal tensors $\text{Tr} = (g_{\parallel}^{\text{cryst}})^2 + 2(g_{\perp}^{\text{cryst}})^2 = g_x^2 + g_y^2 + g_z^2$. We have found that within ± 0.01 error the molecular g -factors can be estimated as $g_z = 2.26$, $g_y = 2.05$ and $g_x = 2.04$. A plot of the crystal g -factors vs. β angle for the above set of the molecular g -factors is shown in Fig. 10 and it satisfies experimental data for $\beta = 78^\circ$. This good fit for both experimental crystal g -factors at the same angle confirms our assumption about $Z = 4$ in the unit cell. Moreover $g_z = 2.26$ is closer to the g_{\parallel} -values measured for solutions (see Table) than the $g_{\parallel} = 2.234$ value calculated for $Z = 2$.

5.2. Molecular structure of $\text{Cu}(3,5\text{-dimethylpyridine})_3(\text{NO}_3)_2$ complex

The $d_{x^2-y^2}$ ground state of a Cu(II) complex appears in elongated octahedral coordination or in a square pyramidal geometry. The position of the ligand field band in the UV-VIS spectrum (Fig. 1) is consistent with these geometries. The three dimethylpyridine ligands coordinate through three nitrogens the central metal ion and a question is how NO_3 -groups are attached to the complex. In this respect the following facts should be taken into consideration: IR data indicate that both monodentate and bidentate nitrato groups exist in the crystal, crystal field symmetry around Cu(II) ion is very close to tetragonal symmetry with only a small rhombic distortion, and there exists a chemical contact between molecules in the crystal as is proved by not very small exchange coupling detected by EPR.

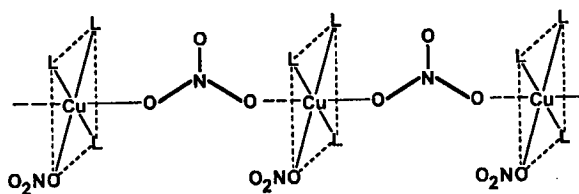


Fig. 11. A proposed molecular structure of $\text{Cu}(3,5\text{-dimethylpyridine})_3(\text{NO}_3)_2$: L denotes N-coordinated 3,5-dimethylpyridine molecule.

The most probable molecular structure which satisfies above requirements are presented in Fig. 11. It is a distorted five-coordination structure with monodentate NO_3 -group in the basal plane and bidentate NO_3 -group in the apical position. The bridging bidentate group is strongly bonded to one of the Cu(II) atom and weakly bonded to the other, which leaves the stereochemistry about copper(II) as essentially square pyramid. The complexes are arranged in polymeric chains as it is suggested by substantial exchange coupling.

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