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Electron paramagnetic resonance study of five-coordinated Cu^{2+} in ethylenediammonium copper(II) diphosphate monohydrate

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Abstract. The results of an electron paramagnetic resonance study of a new product, namely ethylenediammonium copper(II) diphosphate monohydrate of chemical formula $\text{Cu}(\text{NH}_3(\text{CH}_2)_2\text{NH}_3)\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$, are presented. The x-ray diffraction has shown the existence of two types of copper(II) coordination polyhedron for each elementary mesh in this compound. Each polyhedron consists of a copper ion surrounded by five oxygenated ligands stoning from two P_2O_7 groups and a water molecule. Fair agreement between these results and those obtained by x-ray diffraction is observed. In particular the organization of oxygen atoms as pyramids with a square plane around the copper(II) ions is confirmed. The existence of two magnetically non-equivalent sites of copper per mesh is evidenced.

1. Introduction

It is well established that bivalent copper(II) can be coordinated with four, five or six ligands (L) [1–4]. The copper(II) ion has an important plasticity which is due to its non-spherical nature [5]. Moreover, its $3d^9$ configuration is often characterized by deformed polyhedra. The fluxional behaviour of some five-coordinated copper(II) complexes was studied by several spectroscopic techniques which were explained on the basis of the pseudo-Jahn–Teller or second-order Jahn–Teller effect with respect to alternative square-based pyramidal (SBP) and trigonal bipyramidal (TBP) geometries [6]. Several studies on copper(II) complexes with a coordination number of five have shown that the geometry of a SBP is slightly more favourable energetically [7–9]. However, intermediate geometries are sometimes observed [9, 10].

Among the numerous techniques of characterization electron paramagnetic resonance (EPR) spectroscopy appears as one of the most powerful for investigating the local symmetry [11, 12]. This technique resorts to the simulation of experimental spectra by theoretical spectra in order to evaluate the spin Hamiltonian parameters. Such parameters are directly correlated with the geometry of the paramagnetic centre site. Nevertheless, when the elementary mesh contains more than one interacting centre, a low-temperature study is

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also needed. Moreover, in the case of a single crystal, the behaviour as a function of the orientation with respect to the magnetic field must be recorded.

Our sample is constituted of small single crystals. Depending on the conditioning, powder spectra or single-crystal orientable spectra can be observed. The density of paramagnetic centres measured by comparison with a standard sample is 2×10^{17} centres g^{-1} . This concentration is high enough to obtain intense EPR spectra.

2. X-ray diffraction characterization

The $Cu(NH_3(CH_2)_2NH_3)P_2O_7 \cdot H_2O$ compound is synthesized as small light-blue crystallites of different shapes and sizes. The x-ray diffraction study [13] has shown that this complex crystallizes in a monoclinic system of space group $P2_1/n$. The elementary mesh is characterized by the parameters $a = 1.1225$ nm, $b = 1.5425$ nm, $c = 1.2218$ nm and $\beta = 92.24^\circ$. The elementary mesh contains two non-equivalent copper polyhedra. Each polyhedron consists of a Cu(II) ion surrounded by five oxygen atoms organized following a geometry similar to that of a SBP (table 1). In these two sites the Cu(II) ion is very near the centre of the base formed by four oxygen ligands from two P_2O_7 groups. The top of the pyramid is occupied by an oxygen atom from a water molecule (figure 1). The distance between the two copper ions is about 0.414 nm.

Table 1. Angles and distances relative to figure 1. θ^i are the angles between Cu-O(*i*) and Cu-O(5) axes where O(5) is the oxygen atom of the water molecule. θ_{SBP}^i and θ_{TBP}^i are the theoretical angles characteristic of the two configurations SBP and TBP.

Ligand	θ_{SBP}^i (degree)	θ_{TBP}^i (degree)	Cu(1)		Cu(2)	
			θ^i (degree)	d_i (nm)	θ^i (degree)	d_i (nm)
O(1)	100	90	94.0	0.195	93.6	0.199
O(2)	100	120	103.1	0.194	103.8	0.200
O(3)	100	90	92.7	0.194	94.5	0.194
O(4)	100	120	88.9	0.192	89.1	0.188
O(5)	0	0	0	0.251	0	0.242

3. Study of the powder

EPR spectra of the powder of ethylenediammonium copper(II) diphosphate monohydrate for temperatures varying from 100 to 300 K were recorded. To simulate these experimental spectra, we used the method described for example in [14]. The room-temperature (300 K) spectrum is assigned to the Cu(II) ion with electron spin $S = \frac{1}{2}$ and nuclear spin $I = \frac{3}{2}$. This spectrum is easily simulated (figure 2) by a theoretical spectrum for a spin Hamiltonian of the form

$$H_s = \beta[g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] + A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) \quad (1)$$

where β is the Bohr magneton, g_{\parallel} and g_{\perp} are the components of the gyromagnetic tensor \mathbf{g} , and A_{\parallel} and A_{\perp} are the components of the hyperfine tensor \mathbf{A} whose principal axes are

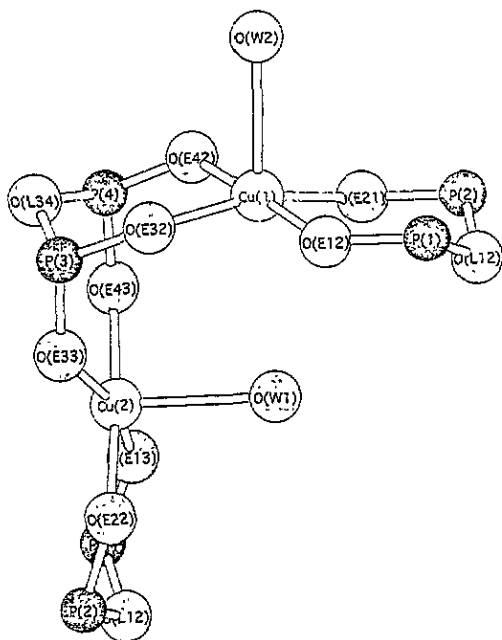


Figure 1. Geometry of the Cu(II) sites determined by x-ray diffraction.

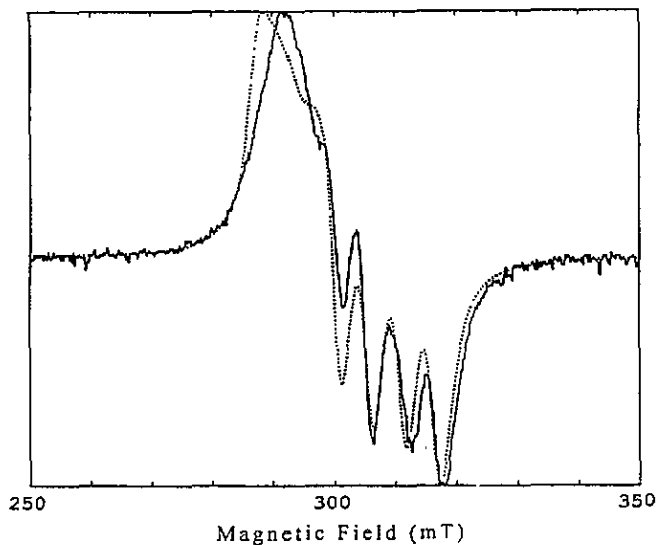


Figure 2. EPR spectrum of the ethylenediammonium copper(II) diphosphate monohydrate powder at 300 K: —, experimental spectrum; ·····, theoretical simulation.

nearly parallel. The values of the parameters given by the simulation are reported in table 2 where ΔH is the linewidth of the correction curve assumed to be Lorentzian.

At a low temperature (100 K) the spectrum appears as a superposition of two different spectra. A satisfactory simulation of the experimental spectrum is obtained for the sum of two theoretical spectra (figure 3) with an axial symmetry, Lorentzian lineshapes and the same weight for the two spectra. The parameters of the simulation are again given in

Table 2. Parameters of the simulation of powder spectra at 100 and 300 K. ΔH_{\parallel} and ΔH_{\perp} are the parallel and perpendicular correction widths, respectively, of lines assumed to have a Lorentzian shape.

T (K)	g_{\parallel}	g_{\perp}	A_{\parallel} (mT)	A_{\perp} (mT)	ΔH_{\parallel} (mT)	H_{\perp} (mT)
100	2.27	2.132	1.0	5.5	3.5	1.3
100	2.19	2.153	1.0	5.8	3.0	2.3
300	2.25	2.13	1.0	5.0	3.2	3.0

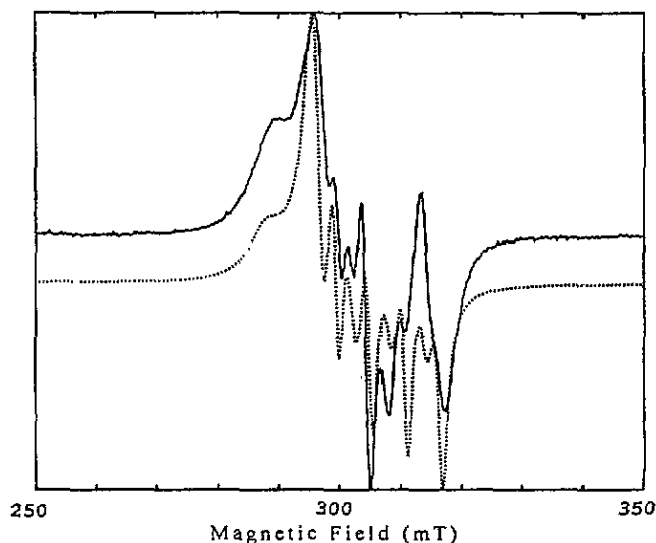


Figure 3. EPR spectrum of the ethylenediammonium copper(II) diphosphate monohydrate powder at 100 K: —, experimental spectrum; ·····, theoretical simulation.

table 2. The spectra obtained at intermediate temperatures are also considered as sums of two spectra.

We cannot obtain a good simulation of each low-temperature experimental spectrum using a single theoretical spectrum with axial or non-axial symmetry even when the quadrupolar interaction is considered. Furthermore, from the value of A_{\perp} (table 2), forbidden transitions were considered, in our case, to have no significant intensity [14].

The possibility of obtaining a good fit with the sum of two theoretical spectra suggests the presence of two magnetically non-equivalent Cu(II) sites in our compound. The coupling between the Cu(II) ions occupying these two sites must be rather small. Indeed it has been shown that, in the presence of coupling with a strong exchange compared with the hyperfine interactions, seven lines ($4I + 1$) should be observed [15, 16]. In our case, eight lines corresponding to the region of g_{\perp} of the experimental spectrum are observed.

Each of these sites possesses an axial symmetry (table 2). The small values of A_{\parallel} indicate that the unpaired electrons are more localized in the vicinity of the ligands in the direction of g_{\parallel} than in the g_{\perp} plane. Whereas the component g_{\parallel} of the gyromagnetic tensor relative to the two sites is sensitive to a temperature variation, the component g_{\perp} does not seem to be affected (figure 4). This result indicates that for both sites the distances between the copper and the ligands in the g_{\perp} plane are more rigid than in the g_{\parallel} direction and

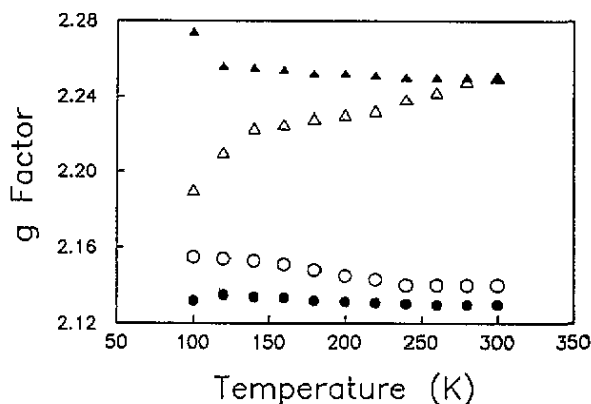


Figure 4. Variation with temperature in the values of $g_{||}$ and g_{\perp} obtained by simulation: ▲, $g_{||}$ for the first site; ●, g_{\perp} for the first site; △, $g_{||}$ for the second site; ○, g_{\perp} for the second site.

therefore the geometry of the copper–ligand system is more stable in this plane.

As the temperature increases, the components $g_{||}$ relative to the two sites become closer until they are equal, whereas the parameters g_{\perp} remain slightly different (figure 4). This result is in agreement with the model resulting from the x-ray diffraction study [13] which shows two sites of copper(II) in $\text{Cu}(\text{NH}_3(\text{CH}_2)_2\text{NH}_3)\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$. In both sites the Cu(II) ion is surrounded by five oxygen atoms. By increasing the temperature, the thermal agitation averages the distances and geometries of both sites which become almost equivalent. Indeed at room temperature the powder spectrum obtained experimentally can be explained with a single site.

4. Study of the single crystal

If the elementary mesh of a single crystal contains two paramagnetic centres occupying two magnetically non-equivalent sites, the EPR spectrum of this single crystal should be composed of an asymmetric line. This asymmetry due to exchange interactions becomes apparent when the two centres are sufficiently near to one another (less than 0.8 nm) [7]. However, it often happens that for particular orientations of the single crystal in the magnetic field, two more or less resolved lines are observed [17–19].

The determination of the components of the \mathbf{g} -tensor of the single crystal is not straightforward since the principal axes of this tensor are different from the crystallographic axes. Moreover a well oriented sample is not always easily achieved, on the basis of only the form of the macroscopic morphology. However, several methods have been proposed to overcome these difficulties [20–23]. Schonland [24] and Ayscough [25] have suggested that, when crystal g -values are determined by rotation studies, the maximum and minimum g -values may be used to calculate the off-diagonal elements of the $[g_{ij}^2]$ matrix. Following the procedure used by Geusic and Carlton Brown [22], the single crystal was rotated in the static magnetic field around three arbitrary axes chosen orthogonal to each other two by two. The origin of the rotation angles θ is chosen so that the magnetic field is parallel to one of the faces of the single crystal. The values of g are measured experimentally for each angle θ and the experimental curves $g_{\text{exp}}(\theta)$ for each of the three directions are fitted to the theoretical expression

$$g_{\text{exp}}^2(\theta) = g_{yy}^2 \cos^2 \theta + g_{zz}^2 \sin^2 \theta + 2g_{yz}^2 \sin \theta \cos \theta. \quad (2)$$

The expressions relative to the two other directions are obtained through circular permutations.

For this study a single crystal whose sketch is given in figure 5 was chosen. The spectra were recorded at a temperature of 90 K in order to reduce the thermal agitation and to obtain a better resolution. Each of the spectra obtained consists in most cases of a slightly asymmetric line. No hyperfine splitting was observed in all orientations of the single crystal. This may be due to the different orientations of the two paramagnetic centres and the two copper isotopes in the crystal [26]. The misalignment between the \mathbf{A} and \mathbf{g} axes may play a role in the absence of the hyperfine splitting [15, 26]. The values of $g_{\text{exp}}^2(\theta)$ are experimentally measured using a DPPH reference standard ($g_0 = 2.0023$). The variations in $g_{\text{exp}}^2(\theta)$ relative to the three axes are represented in figure 6. Simulation by expressions such as (2) allows the determination of the $[\mathbf{g}^2]$ -matrix elements from which the principal values of the \mathbf{g} -tensor of the single crystal are deduced. The values $g_1 = 2.228$, $g_2 = 2.187$ and $g_3 = 2.063$ are found in our case.

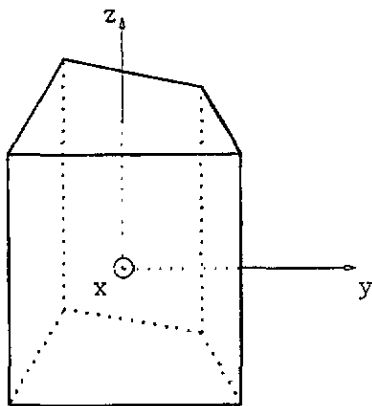


Figure 5. Morphology of ethylenediammonium copper(II) diphosphate monohydrate single crystal used in this study

The cooperative parameters g of the two paramagnetic centres are given by [7]

$$g_{\parallel} = g_1 = 2.228 \quad g_{\perp} = \frac{1}{2}(g_2 + g_3) = 2.125. \quad (3)$$

These values are almost the same as those obtained with the 300 K powder spectrum (table 2). They are also not very different from the arithmetical average of the parameters g_{\parallel} and g_{\perp} obtained from the 100 K powder spectrum ($g_{\parallel} = 2.230$ and $g_{\perp} = 2.142$). Indeed, in the case of two non-equivalent ions in the unit cell, the g -value of the unified peak is given by $g = \frac{1}{2}(g' + g'')$ where g' and g'' are the g -values for each ion when the exchange coupling becomes negligible [23].

In view of the experimental uncertainties, the agreement between the two sets of parameters obtained from powder and from single-crystal studies is quite satisfactory. Indeed, the very small dimensions of the crystal leads to a slight misalignment when it is mounted. Furthermore, as a result of weak exchange, a fit to the experimental spectrum of the theoretical powder spectrum assuming a Lorentzian lineshape is not perfect. However, it can be improved by introducing g -factors and principle linewidth values slightly different from those determined in single-crystal measurements [27].

Knowledge of the principal components of the \mathbf{g} -tensor of the single crystal allows the determination of the angle 2γ between the g_{\perp} directions of the two sites [7]. The value of

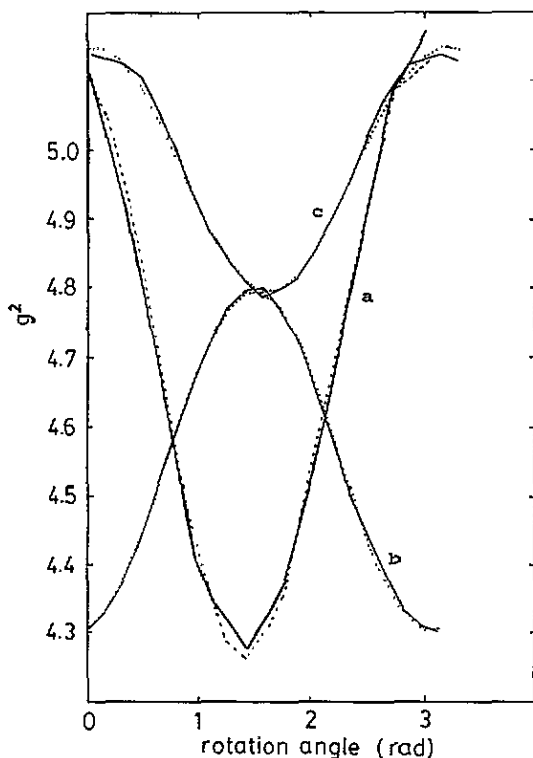


Figure 6. Variation in g_{exp} with the single-crystal orientation for rotations around the x axis (curve a), y axis (curve b) and z axis (curve c): —, experimental; ·····, theoretical.

this angle is given by

$$\cos(2\gamma) = \frac{g_1 - g_2}{g_1 + g_2 - 2g_3} \quad (4)$$

From the experimental values of the components of the \mathbf{g} -tensor the angle between the tetragonal axis of the two sites is found to be 74° . This value does not agree closely with that of the angle between the two quaternary axes of the crystallographic sites, which is about $92^\circ (\simeq \beta)$. This result is not unexpected since magnetic axes are not the same as crystallographic axes [7].

For some orientations of the single crystal in the magnetic field, marked asymmetry was observed and even the presence of two lines. This result confirms the presence of two sites of the copper in the elementary mesh of $\text{Cu}(\text{NH}_3(\text{CH}_2)_2\text{NH}_3)\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$. The simulation of these spectra by the sum of two Gaussian or two Lorentzian lines appeared impossible. This suggests that both lines are coupled together. The sites relative to both lines interact with each other and therefore a spin exchange between the two copper ions exists. This coupling by exchange interaction remains relatively weak since the two lines do not completely overlap. To confirm this hypothesis the parameter J of the exchange interaction $J S_a S_b$, where S_a and S_b are the electronic spin operators of the Cu^{2+} ions occupying the two sites, has been evaluated. When this interaction is present, the shape of the spectrum can be determined by solving the generalized Bloch equations [27–30]. The experimental spectrum is then described by the theoretical expression

$$Y(B) = N \{ [W_2 - 2(B - B_0)J] (W_1^2 + W_2^2) - 4[(B - B_0)W_2 + (\Gamma_0 + 2)W_1] \\ \times [(B - B_0)W_1 - (\Gamma_0 + J)W_2] \} (W_1^2 + W_2^2) \quad (5)$$

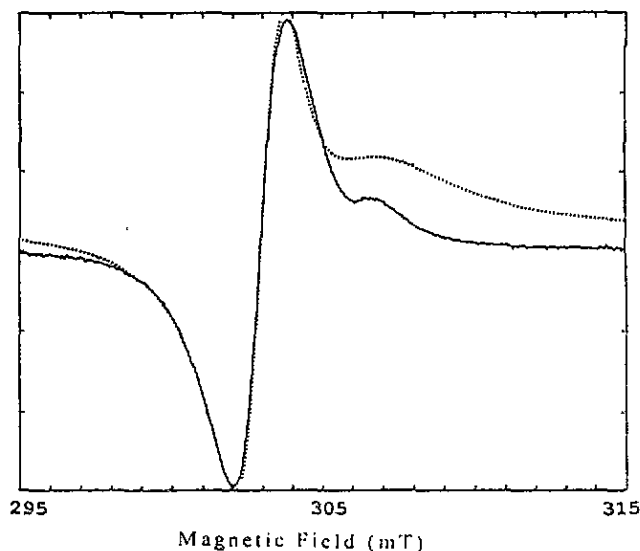


Figure 7. EPR spectrum of the single crystal in an arbitrary orientation: —, experimental; ·····, theoretical simulation.

with

$$\begin{aligned}
 W_1 &= (B - B_a)(B - B_b) - (\Gamma_a + J)(\Gamma_b + J) + J^2 \\
 W_2 &= (B - B_a)(B - B_b) - (\Gamma_a + J)(\Gamma_b + J).
 \end{aligned}
 \tag{6}$$

The parameter N is a normalization factor which depends on the total number of spins in the sample, the Γ_i are the linewidths at half-height of the lines assumed to be Lorentzian ($J \rightarrow 0$). $\Gamma_0 = (\Gamma_a + \Gamma_b)/2$ and $B_0 = (B_a - B_b)/2$. B_a and B_b are the positions of the two lines relative to the two sites. All parameters in the expression for $Y(B)$ are expressed in teslas.

The best fit (figure 7) is obtained for the values $B_a = 0.3029$ T, $B_b = 0.3053$ T, $\Gamma_a = 1.67$ mT, $\Gamma_b = 3.0$ mT and $J = 0.18$ mT. The J -value in ethylenediammonium copper(II) diphosphate monohydrate is not large. So the contributions of the dipole-dipole interaction between the two paramagnetic centres to the EPR parameters are negligible [32, 33]. The value obtained for the J -parameter of the exchange interaction is clearly lower than the hyperfine interaction (table 2). It is also low compared with values found for other copper(II) complexes [28–31]. This may be due to the relatively important distance between the two ions (about 0.414 nm) and the enclosure of each ion by its five oxygen ligands. It is most likely that the coupling between the two ion Cu^{2+} occupying the two sites occurs as a result of superexchange through the ligands. This result justifies the simulation of the powder spectra obtained at low temperatures by the sum of two distinct theoretical spectra.

It is known that Cu(II)L_5 suffers a second-order Jahn–Teller or pseudo-Jahn–Teller effect [6]. The configuration will be unstable, alternating spontaneously between the two limiting configurations: SBP and TBP. The values obtained for g for the simulation of all experimental spectra ($g_{\parallel} > g_{\perp} > g_0$) indicate that the Cu(II) ion is probably in its fundamental state $d_{z^2-x^2}$ which is consistent with the geometry of a SBP [7]. Indeed the expressions for g_{\parallel}

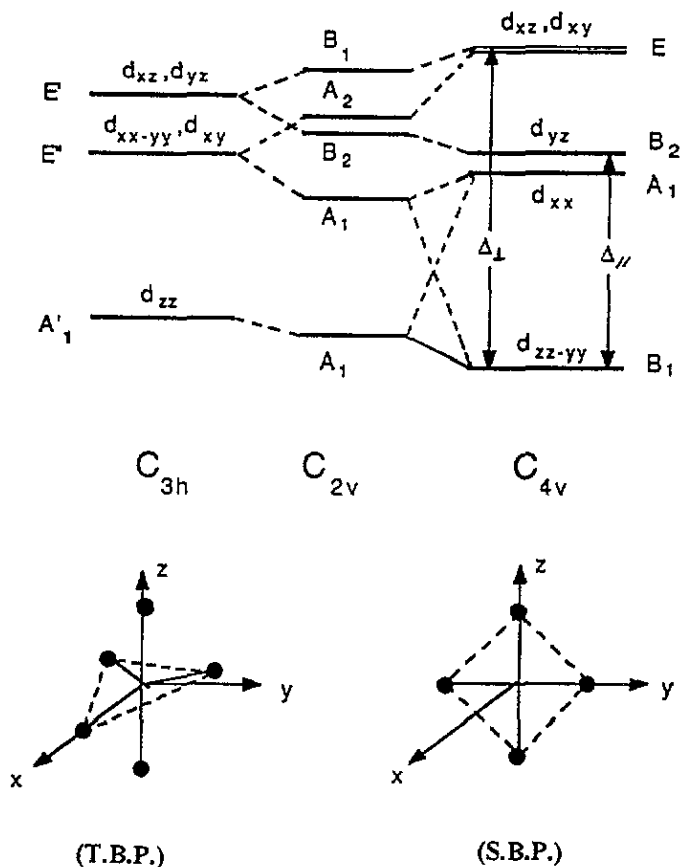


Figure 8. Electronic levels of the Cu^{2+} ion within the configurations SBP and TBP.

and g_{\perp} relative to both configurations are, for TBP,

$$\begin{aligned} g_z &= g_{\parallel} = g_0 \\ g_x &= g_y = g_{\perp} = g_0 + 6u_{\perp} \end{aligned} \quad (7)$$

and, for SBP,

$$\begin{aligned} g_x &= g_{\parallel} = g_0 + 8u_{\parallel} \\ g_y &= g_z = g_{\perp} = g_0 + 2u_{\perp} \end{aligned} \quad (8)$$

where the parameters u_i are defined by

$$u_i = k_i \lambda_0 / \Delta_i \quad (i \equiv \parallel \text{ or } \perp) \quad (9)$$

with $\Delta_{\parallel} = E(\text{B}_2) - E(\text{B}_1)$ and $\Delta_{\perp} = E(\text{E}) - E(\text{B}_1)$ for the C_{4v} symmetry of SBP and $\Delta_{\parallel} = E(\text{E}') - E(\text{A}'_1)$ and $\Delta_{\perp} = E(\text{E}'') - E(\text{A}'_1)$ for the D_{3h} symmetry of TBP (figure 8). The factors k_i are the covalence parameters ($k_{\parallel} = k_{\perp} = 0.7$) and λ_0 is the spin-orbit coupling constant in the free ion equal to 830 cm^{-1} for $\text{Cu}(\text{II})$. The $E(\text{X})$ are the energies of the electronic states X of the $\text{Cu}(\text{II})$ ion which may be obtained from the ligand-field spectra. The notation for the electronic state X is the group theory notation.

5. Conclusion

The parameters of the spin Hamiltonian have been determined by simulating EPR spectra of ethylenediammonium copper(II) diphosphate monohydrate powder. The study leads to the conclusion that two copper sites, which are magnetically non-equivalent in the elementary mesh exist. In each of the sites, the copper is probably in a $d_{z^2-x^2}$ state and occupies the centre of a SBP formed by five oxygen ligands. The bonding of the Cu(II) ion with the two bidental P_2O_7 groups enhances the stability of this configuration toward a second-order Jahn–Teller effect.

The very low value of the exchange interaction parameter J shows that the Cu(II) ions occupying the two sites are not strongly coupled. The exchange of the electronic spins between the two ions is established probably through the ligands.

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