

Effects of non-collinear fine and hyperfine structure on the zero-field electron magnetic resonance of $[\text{Cu}_2(\text{pmdien})_2(\text{N}_3)_2][\text{BPh}_4]_2$

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The zero-field electron magnetic spectrum of $[\text{Cu}_2(\text{pmdien})_2(\text{N}_3)_2][\text{BPh}_4]_2$ has been analysed in terms of an electron spin triplet interacting with two equivalent nuclear spin quartets. The effect of non-collinear zero-field splitting and hyperfine tensors on the transition frequencies is emphasized for this particular spin system. The Euler rotation angles α and γ have little effect on the spectrum whereas $\beta \neq 0$ leads to an effective reduction in A_z for the $D - E$ and $2E$ branches of the triplet spectrum but has no effect on the $D + E$ branch. Least-squares analysis produced spin-Hamiltonian parameters $|D| = 2546.3$ MHz, $|E| = 450.1$ MHz, $|A_z| = 261.5$ MHz and the angle $\beta = 23.9^\circ$.

It has been shown that the application of zero-field electron magnetic resonance (ZFEMR) can provide accurate and more direct determination of the values of spin-Hamiltonian parameters for transition-metal ions doped into host lattices.¹⁻⁴ Some of the advantages of ZFEMR in this regard are that field-dependent terms, the g matrix and its orientation with respect to other parameter matrices in particular, are removed from the spin Hamiltonian, thus significantly reducing the number of parameters required to describe the spectrum, and there is no orientational dependence of an applied magnetic field.⁵ A natural extension of this earlier work is the study of high-nuclearity transition-metal complexes where, in general, multiple frequency spectroscopy is almost always required to determine all of the parameters in the spin Hamiltonian.⁶ Advances in the design of our spectrometer and a new tunable resonator has increased the sensitivity to the point where only a small amount of compound is required, typically 10 mg. A recent report on the spectra of a series of copper carboxylates demonstrates the applicability of this technique to transition-metal clusters.^{7,8}

In this article we report the ZFEMR spectrum of $[\text{Cu}_2(\text{pmdien})_2(\text{N}_3)_2][\text{BPh}_4]_2$ where *pmdien* is *N,N,N',N'',N'''*-penta-methyldiethylenetriamine. The variety of bridging modes exhibited by the azide ligand has made it a valuable tool to those involved in the synthesis of new and interesting molecular-based magnetic materials.^{9,10} Copper dimers bridged by azide ligands are also of interest since the magnetic exchange interaction is known to have a large anisotropic contribution. In fact in $[\text{Cu}_2(\text{pmdien})_2(\text{N}_3)_2][\text{BPh}_4]_2$ Banci *et al.*¹¹ demonstrated that the anisotropic exchange was the dominant contribution to the zero-field splitting.

Experimental

Sample preparation

The compound $[\text{Cu}_2(\text{pmdien})_2(\text{N}_3)_2][\text{BPh}_4]_2$ was prepared according to the procedure outlined by Felthouse and Hendrickson.¹² The salt $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.84 g, 5 mmol) was dissolved in water (10 cm³). To this solution *pmdien* (0.87 g, 5 mmol) was added. This was accompanied by a change from pale blue to a very deep blue. The solution was stirred for several minutes and then NaN_3 (1.64 g, 25 mmol) dissolved in water (15 cm³) was added. The solution changed to a deep green. After allowing it to stand for 1 h it was filtered to remove a precipitate of $[\text{Cu}_2(\text{pmdien})_2(\text{N}_3)_2][\text{ClO}_4]_2$. An aqueous solution of NaBPh_4 (0.5 g)

was added to the filtered solution. A green precipitate formed immediately, which was collected by vacuum filtration and washed with water and diethyl ether. The product was recrystallized from acetone. Elemental analyses were performed by the Australian National University analytical service (Found: C, 66.6; H, 7.5; Cu, 10.4; N, 14.0. Calc. for $\text{C}_{33}\text{H}_{43}\text{BCuN}_6$: C, 66.3; H, 7.3; Cu, 10.6; N, 14.0%).

Spectroscopy

The EMR spectra were recorded on a Varian V-4502 EPR spectrometer equipped with an Oxford instruments ESR900 continuous-flow cryostat, at 5 K, microwave frequency 9.25 GHz and with several levels of microwave power between 40 and 4 mW.

The ZFEMR spectra were recorded using previously described apparatus.⁸ The spectra of $[\text{Cu}_2(\text{pmdien})_2(\text{N}_3)_2][\text{BPh}_4]_2$ were recorded at 6.5 ± 0.5 K with a modulation field of 2 mT. Temperature was measured by a Au/0.07% Fe chromel thermocouple placed in the top of the resonator shield. It is difficult accurately to measure the temperature in the sample region as any metal in the vicinity of the resonator can destroy its quality factor, Q .¹³ The frequency range investigated was spanned by a single loop-gap resonator. The microwave sources were a Hewlett-Packard 8620C sweep oscillator with a HP86222A radiofrequency plug-in for the 1–2 GHz range and a HP86290C one for the 2–4 GHz range. The 1–2 GHz portion of the spectrum was collected with microwave power 1 mW and the 2–4 GHz range with 10 mW. The frequency was measured by a Hewlett-Packard 5351B frequency counter which was connected to the computer controller *via* a general purpose interface bus (GPIB).

Simulations

Computer simulations of ZFEMR spectra were performed using the program ZFEMR which was developed in this laboratory to take advantage of the simplifications that ZFEMR has over the usual EMR technique. The simulations are calculated as the difference between the zero-field absorption spectrum and a Zeeman spectrum where the applied field is the peak field of the bidirectional square-wave modulation. Least-squares fits to the observed spectrum were calculated using simplex and Levenberg–Marquardt routines.^{14,15} Computer simulations of EMR spectra were calculated using a program written in this laboratory.

Table 1 Results of least-squares fitting to the observed ZFEMR spectrum. The parameters A_x , A_y , α and γ are poorly defined and no error estimates are given for these; the values listed here are one of a number of sets that gave equally good fits; ρ is the half-width at half-height of a Gaussian function used in the simulations

D/MHz	E/MHz	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$	A_x/MHz	A_y/MHz	A_z/MHz	ρ	Ref.
2546.3(4)	450.1(5)	107	23.9(3)	232	69	31	261.5(3)	31.6(4)	This work
2560	444	98	23.3	265	69		279		11
2610	486						233		12

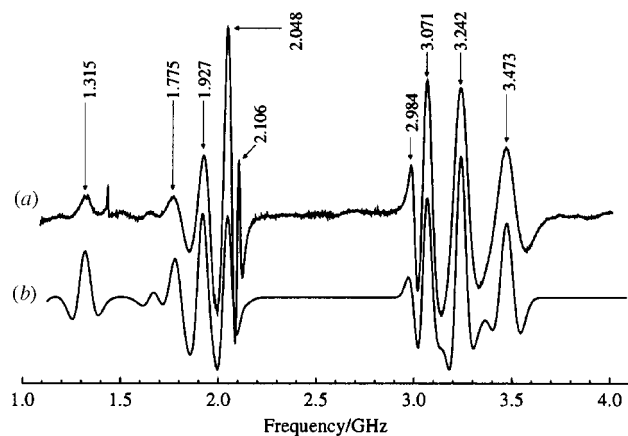


Fig. 1 (a) Powder ZFEMR spectrum of $[\text{Cu}_2(\text{pmdien})_2(\text{N}_3)_2][\text{BPh}_4]_2$ measured at 6.5 K and modulation field 2 mT. The 1–2 GHz range has been scaled using a portion where the two spectra overlapped. (b) The simulated spectrum using the spin-Hamiltonian parameters listed in Table 1

Results

The ZFEMR spectrum of $[\text{Cu}_2(\text{pmdien})_2(\text{N}_3)_2][\text{BPh}_4]_2$ is shown in Fig. 1; the frequencies of the most intense peaks have been labelled. The sharp peak at approximately 1.4 GHz is an instrumental artifact. The spectrum can be divided into two distinct regions following the behaviour of a triplet state with zero-field splitting. The four large peaks in the range 2.8–3.6 GHz can be thought of as arising from the D + E branch of the triplet state, the observed structure being the result of hyperfine interactions. The D – E branch lies in the range 1.7–2.2 GHz. The peak at 1.315 GHz is part of the 2E branch.

The data were modelled using a spin Hamiltonian of the form (1) where I_1 and I_2 are the nuclear spin operators for the

$$\mathcal{H} = S \cdot D \cdot S + S \cdot A \cdot I_1 + S \cdot A \cdot I_2 \quad (1)$$

two Cu^{2+} ions. The simulation shown in Fig. 1 reproduces the experimental spectrum except for the $M_1 + M_2 = 0, 1$ peaks of the D – E branch. This part of the spectrum was reproducible with different samples and various levels of microwave power. Nuclear quadrupole coupling was one possible explanation for the poor agreement between the calculated and experimental spectra in this region. However, calculations of spectra including nuclear quadrupole coupling did not improve the calculated spectrum. Furthermore, simulations showed that nuclear quadrupole coupling had no effect on the calculated spectrum unless unrealistically large values for the coupling constant were used.

The crystal structure¹² shows that the copper ions are related by a centre of inversion, therefore the hyperfine constants for each Cu^{2+} ion were set equal to each other. This left eight parameters in the model: the zero-field splitting terms D and E ; the copper hyperfine parameters A_x , A_y and A_z ; and three angles α , β and γ which are the Euler rotation angles describing the transformation from the coordinate frame of the zero-field splitting to the coordinate system of the hyperfine tensor. The results of least-squares fitting procedures are

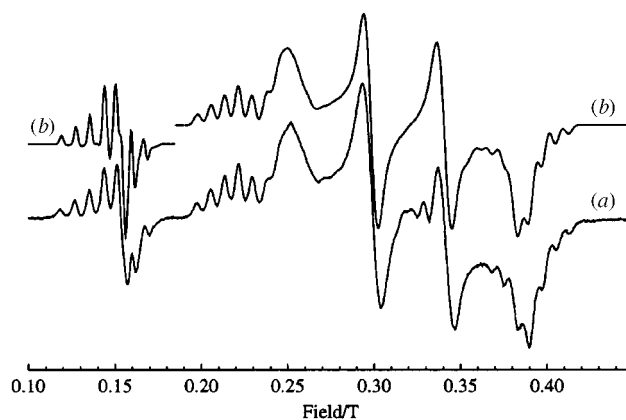


Fig. 2 Experimental (a) EMR spectrum measured at 5 K, 14 mW and frequency = 9.3028 GHz. The simulated spectrum (b) was calculated using $g_x = 2.056$, $g_y = 2.025$, $g_z = 2.20$ and with the field-independent parameters given in Table 1

given in Table 1 along with parameter values determined from powder¹² and single-crystal¹¹ EMR. The parameters A_x , A_y , α and γ are poorly defined and several sets of values for these parameters produced equally good fits to the experimental spectrum. However, attempts at eliminating some of these parameters from the refinements produced worse fits. This suggests that there exists some form of correlation between these parameters. An example is that when $A_x = A_y$, that is the hyperfine interaction is axial, then the angle γ is redundant. The modulation field in our ZFEMR spectrometer is usually less than 3 mT, hence the Zeeman interaction is very small and anisotropy in the g values would need to be very large to have any effect on the ZFEMR spectrum. However the g values are needed in the calculation of the Zeeman spectrum which were taken from Banci *et al.*¹¹ and were assumed to be parallel to the hyperfine axes.

The EMR spectrum of $[\text{Cu}_2(\text{pmdien})_2(\text{N}_3)_2][\text{BPh}_4]_2$ of the same sample as used in the ZFEMR is shown in Fig. 2. Felthouse and Hendrickson¹² reported that the powder EMR spectrum was subject to saturation effects at low temperatures, however our measurements of the EMR spectrum of $[\text{Cu}_2(\text{pmdien})_2(\text{N}_3)_2][\text{BPh}_4]_2$ did not show any saturation effects on varying the microwave powder between 40 and 4 mW. We note, however, that the signal at 5 K is very strong and only a small sample was used in order to avoid operating the crystal detector in a region of non-linear response.

The parameters obtained from the analysis of the ZFEMR spectrum have been used to simulate the powder EMR spectrum of $[\text{Cu}_2(\text{pmdien})_2(\text{N}_3)_2][\text{BPh}_4]_2$. The field-independent terms in the spin-Hamiltonian parameters were fixed at the values obtained from the analysis of the ZFEMR spectrum and only g values were altered. The simulation presented in Fig. 2 was calculated using parameters $g_x = 2.056$, $g_y = 2.025$ and $g_z = 2.20$. The field-independent terms in the Hamiltonian, such as zero-field splitting and hyperfine structure, are given in Table 1. The powder EMR spectrum like the ZFEMR was insensitive to the angles α and γ which were fixed at 270 and 90° respectively. The intensity of the half-field transitions of the simulation in Fig. 2 has been scaled by a factor of 1/4.

Discussion

In the strong exchange limit, that is when the isotropic magnetic exchange interaction is much larger than the other terms in the Hamiltonian, the observed spectrum can be treated as a superposition of spectra arising from each of the total spin states.¹⁶ Isotropic exchange between two Cu²⁺ ions results in a singlet state and a triplet state; the singlet state is the ground state when the exchange interaction is antiferromagnetic. Therefore the simplest way in which to describe ZFEMR spectra of copper dimers with strong magnetic exchange is in terms of a triplet state with zero-field splitting. The zero-field splitting may arise from both dipole-dipole interactions between the two Cu²⁺ ions and from anisotropy in the magnetic exchange interaction. In zero field the degeneracy of a triplet is removed by the zero-field splitting term, resulting in three sub-states, equations (2)–(4), with eigenvalues $D + E$, $D - E$ and 0. In

$$|+\rangle = (1/\sqrt{2})(|1\rangle + |-1\rangle) \quad (2)$$

$$|-\rangle = (1/\sqrt{2})(|1\rangle - |-1\rangle) \quad (3)$$

$$|0\rangle = |0\rangle \quad (4)$$

zero field the probability for a transition between two states i and j is given by expression (5). This gives rise to the selection

$$P_{ij} \propto |\langle i|g_x S_x|j\rangle|^2 + |\langle i|g_y S_y|j\rangle|^2 + |\langle i|g_z S_z|j\rangle|^2 \quad (5)$$

rules $\Delta M_S = 0, \pm 1$ and results in three possible transitions of equal probability which are conveniently labeled according to the transition energy as $D - E$, $D + E$ and $2E$. The $2E$ transition corresponds to a transition from the $|+\rangle$ to the $|-\rangle$ state and arises from the $\Delta M_S = 0$ selection rule. In EMR the use of basis functions corresponding to the high-field limit has led to this transition being referred to as a $\Delta M_S = 2$ transition.

The introduction of Cu²⁺ hyperfine interactions splits each of the transitions into four, and the selection rule becomes $\Delta M_S = 0, \pm 1$, $\Delta M_1 = 0$, $\Delta M_2 = 0$ where M_1 and M_2 are the nuclear magnetic quantum numbers for each of the Cu²⁺ ions. Strictly speaking, transitions which satisfy $\Delta M_S = 0$, $\Delta M_1 = 0$, ± 1 , $\Delta M_2 = 0$ are allowed but the intensity for such transitions is proportional to the square of the nuclear magnetic moment and hence weaker than transitions involving electron spin by a factor $(g_N \mu_N / g_e \mu_B)^2 \approx 10^{-7}$.

In previous work on the ZFEMR of copper carboxylates we employed a model which assumed the x and y components of the hyperfine interaction were zero and that the principal directions of the zero-field splitting and hyperfine tensors were collinear.⁸ For the purposes of discussion we refer to this as the 'simple model'. Expressions for the transition frequencies are given in equations (6) and (7). The simple model proved to be

$$\Delta \varepsilon_{D \pm E} = D \pm [A_{\parallel}^2(M_1 + M_2)^2 + E^2]^{\frac{1}{2}} \quad (6)$$

$$\Delta \varepsilon_{2E} = 2[A_{\parallel}^2(M_1 + M_2)^2 + E^2]^{\frac{1}{2}} \quad (7)$$

very effective in the sense that it accurately reproduced the transition frequencies of copper carboxylates, provided a means of assigning transitions according to the value of $M_1 + M_2$ and also provided a simple explanation for the low intensity of the $M_1 + M_2 = 0$ transitions.

According to equation (6), transitions with $M_1 + M_2 = 0$ are separated by $2E$ and are centered about D . The small peaks at 2.106 and 2.984 GHz are the $M_1 + M_2 = 0$ transitions of the $D - E$ and $D + E$ branches respectively. Likewise the peaks at 2.048 and 2.3071 GHz are the $M_1 + M_2 = 1$ transitions and so on for the remaining peaks of the $D - E$ and $D + E$ branches. The small peak at 1.68 GHz and the peak at 1.315 GHz are part of the $2E$ branch of the spectrum and are assigned to the

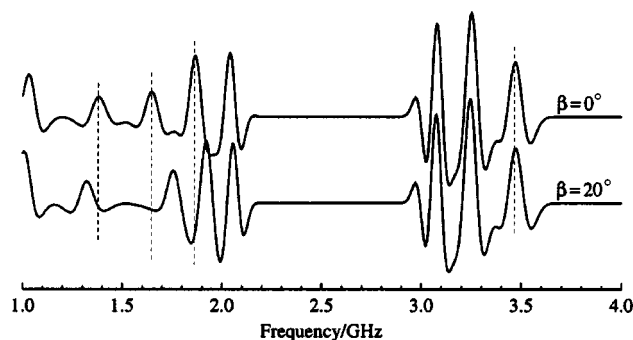


Fig. 3 Simulations of the ZFEMR spectrum using the simple model but with the constraint that the principal directions of D and A are parallel removed. The spin-Hamiltonian parameters used to calculate the simulations are $D = 2.56$ GHz, $E = 0.444$ GHz, $A_{\parallel} = 0.26$ GHz and the linewidth is 35 MHz. The Euler angles relating the D tensor to the A matrix are $\alpha = 90$, $\beta = 0, 20$ and $\gamma = 270^\circ$

$M_1 + M_2 = 3$ and 2 transitions respectively. The factor of 2 in equation (7) explains the larger hyperfine splitting in the $2E$ branch compared to the $D - E$ and $D + E$ branches.

Using the expressions (6) and (7) and the values of D , E and A_{\parallel} given in Table 1, the calculated transition frequencies for the $D + E$ branch of the spectrum are 2.996, 3.066, 3.236 and 3.451 GHz, which agree well with the peak positions shown in Fig. 1. However, this simple model fails to give the correct transition frequencies for the $D - E$ and $2E$ branches of the spectrum. The calculated values 2.096, 2.026, 1.856 and 1.642 GHz for the $D - E$ branch do not compare well with the observed peak positions. The difference between the observed and calculated peak positions increases from 10 MHz for the $M_1 + M_2 = 0$ transition to 133 MHz for the $M_1 + M_2 = 3$ transition. The reason for the failure of the simple model is that the assumption that the hyperfine and zero-field splitting tensors are parallel is not valid in this compound.

From the results of single-crystal EMR spectra Banci *et al.*¹¹ found the x axes of the zero-field splitting tensor and hyperfine matrix are almost parallel. The principal z axis of D is related to the z axis of g by a 23° rotation about the common x axis. A rotation in one plane at Q band indicated that the g and A tensors are parallel. That is, the zero-field splitting and hyperfine interactions are not collinear but are related by the Euler angles $\alpha = 98$, $\beta = 23$ and $\gamma = 265^\circ$.

Two simulations with $\alpha = 90$, $\gamma = 270$ and $\beta = 0$ (a) and 23° (b) are presented in Fig. 3. Comparison of these two figures shows the striking effect of this rotation angle on the calculated position of the peaks belonging to the $D - E$ and $2E$ branches of the spectrum. An increase in this angle can be thought of as producing an effective reduction in the value of A_{\parallel} . For reasons which we do not pursue in this paper the $D + E$ branch of the spectrum is largely independent of the angle β .

The $D - E$ branch of the spectrum can be reproduced with an effective $A_{\parallel}^{\text{eff}} = 205$ MHz. Following the simple model described above in which $A_{\perp} = 0$ it is a simple matter to show that $A_{\parallel}^{\text{eff}} = A_{\parallel} \cos^2 \beta$. This corresponds to an angle of 27° between the principal z axes of the zero-field splitting and the hyperfine interactions.

In the analysis of the results it was found that the angles α and γ were poorly defined and correlated with the values of A_x and A_y . Therefore it is worth mentioning the significance of the Euler angles to this particular spin system. First it must be mentioned that the rotation operation $R(\gamma)R(\beta)R(\alpha)$ transforms a coordinate in the reference frame of the principal axes of the zero-field splitting tensor to the reference frame of the hyperfine matrix. It is well known that the EMR of Cu²⁺ in a square-planar environment exhibits hyperfine structure that is strongly axial, that is $A_x \approx A_y \ll A_z$. A consequence of this is that there is no unique direction which clearly defines the direction of the x and y axes of the hyperfine matrix. In terms of the Euler

rotations this means the angle γ is redundant. The angles α and β correspond to the polar coordinates φ and θ respectively, where θ is the angle between the z axes of D and A and φ that made by the zero-field x axis and the projection of the hyperfine z axis onto the zero-field splitting xy plane. Since the orthorhombic component in D is large, we expected α would be a well determined parameter but this did not turn out to be the case.

Given the discrepancy in the field-independent parameters of the spin Hamiltonian obtained by Banci *et al.*¹¹ and from our analysis of the ZFEMR we have simulated the EMR spectrum of $[\text{Cu}_2(\text{pmdien})_2(\text{N}_3)_2][\text{BPh}_4]_2$. A comparison between the observed and calculated spectrum is shown in Fig. 2. Since the discrepancy between the zero-field splitting parameters is the order of only 10–20 MHz large differences between the g values are not expected, however changes to the principal g values were required to improve the agreement between the simulated and calculated spectra. Banci *et al.* reported that the spin-Hamiltonian parameters were temperature sensitive over the range 4–140 K with variations in the g values of up to 0.03 but it is not expected that variations of a few degrees would give rise to any significant variation in the g values.

Conclusion

We have employed the under utilized technique of zero-field electron magnetic resonance spectroscopy accurately to determine some of the field-independent terms in the spin Hamiltonian. The model used to simulate the experimental spectrum treated the system within the strong-exchange limit, that is it assumed the mixing between the singlet and triplet states to be negligible. The effect of non-coincident zero-field splitting and hyperfine tensors on the ZFEMR spectrum was investigated and found to lead to an effective reduction of A_z in the $D - E$ and $2E$ branches of the spectrum whereas the $D + E$ branch was largely unaffected.

Least-squares analysis of the spectrum produced accurate values of D , E and A_z all of which were significantly different from the values determined from powder and single-crystal EMR. However the values determined here are much closer than those given by Banci *et al.*¹¹ obtained from the single-crystal EMR. One explanation for the difference between the parameters given by Banci *et al.* and those determined in this

work is misalignment of the crystal in the magnetic field. This highlights one of the strengths of this technique, in that the absence of an applied field removes any orientation dependence of the sample thus removing a possible source of error.

Finally the powder EMR spectrum was reinvestigated using the parameters determined from the ZFEMR to determine the field-dependent terms of the Hamiltonian.

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