High frequency electron paramagnetic resonance (HFEPR) study of a high spin Co(II) complex

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Abstract

Variable high-frequency electron paramagnetic resonance data were collected for a single crystal of [Zn(hmp)(dmb)Cl] 4 (1) doped with a small quantity of high spin Co(II), where dmb is 3,3-dimethyl-1-butanol and hmp- is the monoanion of 2-hydroxy-methylpyridine. The lack of solvent in the lattice of complex 1 results in very little disorder. Consequently, the EPR spectra are extremely sharp, enabling precise comparisons with theoretical simulations. We find the ground state of the Co(II) ions to be an effective spin $S^\prime = 1/2$ Kramers’ doublet with a highly anisotropic $g$-tensor. The anisotropy is found to be of the easy-axis type, with the single-ion easy axis directions tilted away from the crystallographic $c$ direction by $58^\circ$. © 2006 Elsevier Ltd. All rights reserved.

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1. Introduction

Single-molecule magnets (SMM) are compounds that possess a large ground state spin value and a significant negative magnetoanisotropy that acts as a barrier to magnetization reversal. Some of the most widely studied of these compounds consist of magnetic cores comprising transition metal ions such as Mn$^{3+}$ and Mn$^{4+}$, Fe$^{2+}$, and Ni$^{2+}$. These materials exhibit a variety of interesting phenomena such as magnetization hysteresis below a characteristic blocking temperature [1–4], quantum tunneling of the magnetization [5,6], and quantum phase interference effects [7].

Detailed high frequency electron paramagnetic resonance (HFEPR) studies of a [Ni(hmp)(dmb)Cl] 4 SMM (Ni 4 ), and a Zn analog doped with a tiny quantity of Ni$^{2+}$, have yielded a complete picture of the quantum magnetization dynamics and zero-field-splitting (zfs) parameters for these systems [8–10]. Two analogous compounds were recently synthesized with Co$^{3+}$ ions replacing the Ni$^{2+}$ ions, the formula for complex 1 being [Zn$_{0.995}$Co$_{0.005}$- (hmp)(dmb)Cl] 4. It was previously shown that the tetranuclear Co complex (Co 4) exhibits weak magnetization hysteresis below about 1 K, suggesting that it could be a SMM [11]. The motivation for the present study is to quantify any anisotropy at the individual Co$^{2+}$ sites, as well as the orientations of the individual Co$^{2+}$ ion magnetic axes with respect to the lattice for complex 1, similar to the work reported for the Ni$^{2+}$ doped Zn complex [8,12]. The ultimate goal is to determine whether the Co 4 complex really is a SMM and, if so, whether its associated zfs parameters can be rationalized in terms of the local anisotropy associated with the individual Co$^{2+}$ ions.

The lack of solvent in the lattice of complex 1 results in very little disorder. Consequently, the HFEPR spectra are extremely sharp, enabling accurate comparisons with theoretical simulations. However, the presence of Co$^{3+}$ adds a level of complexity not found for Ni$^{2+}$, due to the strong
spin-orbit coupling in the former [13]. Therefore, the usual giant spin approximation must be modified to account for the orbital contribution to the magnetic properties. However, as we shall see, only the lowest Kramers’ doublet contributes to the low-temperature (<20 K) HFEPR spectrum of complex 1, thus reducing the problem to that of an effective spin \( S' = 1/2 \). The magnetic properties can then be simulated in terms of a simple Zeeman Hamiltonian, \( \hat{H} = \mu_0 \mathbf{S} \cdot \mathbf{g}^\prime \cdot \mathbf{B} \), where \( \mathbf{g}^\prime \) represents an effective Landé \( g \)-tensor associated with the effective spin \( S' = 1/2 \). We also show from angle-dependent single-crystal HFEPR measurements that the easy-axis associated with each Co\(^{2+} \) ion is significantly tilted away from the \( c \)-axis of the crystal. More detailed studies of both complexes will be discussed in a future paper [14].

2. Experimental details

Single-crystal HFEPR measurements were carried out using a sensitive cavity perturbation technique. A millimeter-wave vector network analyzer (MVNA) acted as both a sensitive cavity perturbation technique. A millimeter-wave vector network analyzer (MVNA) acted as both a sensitive cavity perturbation technique. A millimeter-wave vector network analyzer (MVNA) acted as both a sensitive cavity perturbation technique. A millimeter-wave vector network analyzer (MVNA) acted as both a sensitive cavity perturbation technique.

Table 1

<table>
<thead>
<tr>
<th>Crystallographic data for [Zn(<em>{3.98})Co(</em>{0.02})(hmp)(_4)(dmb)(_4)Cl(_4)]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
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<tr>
<td><strong>Temperature (K)</strong></td>
</tr>
<tr>
<td><strong>Wavelength (Å)</strong></td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
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<tr>
<td><strong>Space group</strong></td>
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<tr>
<td><strong>Unit cell dimensions</strong></td>
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<tr>
<td>( a ) (Å)</td>
</tr>
<tr>
<td>( b ) (Å)</td>
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<tr>
<td>( c ) (Å)</td>
</tr>
<tr>
<td>( \alpha ) (°)</td>
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<tr>
<td>( \beta ) (°)</td>
</tr>
<tr>
<td>( \gamma ) (°)</td>
</tr>
</tbody>
</table>

**Volume (Å\(^3\))** |
5837.3(5)

**Z, Z’** |
4, 0.25

**Density (calculated) (g/cm\(^3\))** |
1.411

**Crystal size (mm\(^3\))** |
0.29 × 0.17 × 0.15

X-ray crystallographic data taken for a single crystal of complex 1.

At the lowest temperatures, one can make the assumption that only the ground state for each Co\(^{2+} \) ion is populated. Furthermore, as we shall see below, the ground state is a well isolated Kramers’ doublet. Thus, each Co\(^{2+} \) ion may be expected to contribute only one peak to the HFEPR spectrum (containing some fine structure due to disorder-induced strain). Thus, assuming the magnetic axes associated with the four possible Co\(^{2+} \) sites on the Zn\(_3\)Co molecule are non-collinear, one should observe four separate HFEPR peaks for arbitrary field orientations (one for each Co\(^{2+} \) site). For field orientations along certain symmetry directions, two or more of these transitions may become degenerate, thus reducing the number of peaks.

Fig. 1 displays frequency-dependent data for complex 1 obtained at 2 K, with the field tilted 32° away from the \( c \)-axis of the crystal in the (100) plane (vide infra, see Fig. 3). The inset to Fig. 1 shows a typical spectrum obtained at a frequency of 51.8 GHz. As can be seen, absorptions are grouped into three clusters. The position of each peak is plotted versus frequency in the main part of the figure for measurements performed on higher-order cavity modes. As can be seen, each peak lies on an absolutely straight line which passes exactly through the origin. Landé \( g \)-factors have been assigned to each of the peaks based on the slope of the straight line through each set of data points. The shapes of the data points (solid and open circles and squares) have been chosen for comparison with Fig. 3 below. We believe the fine structures are caused by disorder induced \( g \)-strain (as was found from similar studies of the Ni/Zn analog [8,10]).

Based on the angle-dependent studies discussed below, we find that the \( g = 4.2 \) branch in Fig. 1 is in fact degenerate, consisting of two HFEPR transitions. This explains the observation of only three peaks. The relative intensities of
the peaks may be understood in terms of the transition rates [18], which depend on the respective Landé g-factors (smaller g-factor, larger transition rate). The fact that each resonance lies on a perfectly straight line is a clear indication that the transitions occur within a very well isolated effective spin $S^\prime = 1/2$ Kramers’ doublet. The anisotropy is contained entirely within the effective Landé g-tensor. Further confirmation comes from the temperature dependence in Fig. 2. These data were obtained for the same frequency and field orientation as the data in Fig. 1; one can see that the field alignment is not precisely the same due to the slight splitting of the degenerate branch. Nevertheless, all peaks increase in intensity upon lowering the temperature, thus confirming the assignment of the ground state as a spin $S^\prime = 1/2$ Kramers’ doublet.

By far the most detailed information comes from angle-dependent studies. For an arbitrary rotation plane each spectrum should consist of four peaks. However, for high symmetry rotation planes there will be degeneracies and some resonance peaks will superimpose upon one another. The highest symmetry direction corresponds to a magnetic field applied along the c-axis of the crystal, where only one peak should be seen. A magnetic field applied at an arbitrary angle within the ab-plane of the crystal will give rise to two peaks. Any misalignments of the sample with respect to the applied field will lift this degeneracy and give rise to up to four major peaks.

The first experiment (rotation 1) involved rotating the magnetic field in the (110) plane from the c-axis to the ab-plane (Fig. 3a). The second experiment (rotation 2) involved rotating the magnetic field within the ab-plane (Fig. 3b). For rotation 1 we observe three resonance branches, which collapse into approximately 1 peak for $\theta = 0^\circ$ (field//c-axis) and approximately two peaks for $\theta = 90^\circ$ (field//ab-plane, 45° from a and b). Since only three branches are observed in Fig. 3a, we must assume that one of them is degenerate (solid circles).

Based on simple geometrical considerations, we can immediately determine the nature of the anisotropy at the individual Co$^{2+}$ sites. Due to the octahedral coordination, we assume the anisotropy will be approximately axial (easy-plane or easy-axis [19]). First of all, it is clear from Fig. 3a that the local magnetic axes are tilted with respect to the crystallographic axes (and, therefore, with respect to each other). Starting with the field along c (Fig. 3a): when one tilts the field away from this symmetry direction, it necessarily tilts away from three of the local z-axes and towards three of the xy-planes; conversely, it tilts towards one of the $z$-axes and away from one of the $xy$-planes. Considering the two-fold degeneracy of the branch represented...
by the solid circles, upon tilting the field away from \( c \) one sees that three of the branches move to higher fields (they become harder), whereas only one moves to lower field (it becomes easier). Therefore, based on the above geometrical consideration, one can conclude that the planes are hard, while the axes are easy, i.e., the anisotropy is of the easy-axis type.

Upon rotating the field over a 180\(^{\circ}\) interval, one is guaranteed to find all four hard planes. These directions correspond to the maxima at \(-90^{\circ}\) (two planes), \(-32^{\circ}\) and \(+32^{\circ}\) (the peak at \(+90^{\circ}\) is equivalent to the one at \(-90^{\circ}\)) in Fig. 3a, and the maxima at \([n \times 90^{\circ}] + 45^{\circ}\) in Fig. 3b, where \( n \) is an integer. Since we observe a degenerate branch in Fig. 3a, this implies that orientation of the field, as it rotates, is the same for both ions contributing to the branch. Thus, the field rotation plane must be perpendicular to the easy-axis tilt plane for these two ions and, therefore, by symmetry, it must be parallel to the easy-axis tilt plane for the other two ions. Therefore, we conclude that the two minima labeled \( z \) correspond precisely to the easy axes. One can then immediately determine that \( g_{z} = 7.80 \) (indicated by blue dashed line). The minimum at \( 0^{\circ} \) in Fig. 3a corresponds to the point of closest approach of the field to the other two easy axes. From the positions of the maxima and minima, we determine that the easy axes (hard planes) are tilted about \( 58^{\circ} \) \((32^{\circ})\) away from the crystallographic \( c \)-axis, and the easy axes are tilted in the \((110)\) and \((1\overline{1}0)\) planes.

It is notable in Fig. 3a that the heights of the maxima at \( \pm90^{\circ} \) and \( \pm32^{\circ} \) are slightly different, corresponding to \( g \)-values close to \( 2.00 \) and \( 2.20 \). This observation implies weak in-plane anisotropy, suggesting a weak orthorhombic distortion at the individual \( \text{Co}^{2+} \) sites. The lesser of the two \( g \)-values corresponds to \( g_{z} \approx 2.00 \) (the hard axis, red dashed line) and the intermediate value to \( g_{z} \approx 2.20 \) (the medium axis, green dashed line).\(^1\) From the hard-plane rotations (Fig. 3b), we see that the maxima coincide with \( g_{z} \approx 2.20 \) in Fig. 3a. Therefore, we can conclude that the medium axes lie along the intersections of the four hard planes, within the \( ab \)-plane of the crystal \([\text{along} (110) \text{and} (1\overline{1}0)]\). The hard axes are, therefore, directed maximally out of the \( ab \)-plane \([\text{with projections also along} (110) \text{and} (1\overline{1}0)]\), tilted \( 32^{\circ} \) away from \( c \). The minima in Fig. 3b correspond to the projection of the easy axis anisotropy onto the \( ab \)-plane, i.e. \( g = g_{z} \times \cos32^{\circ} = 6.61 \) (marked by horizontal black dashed line). Finally, the vertical dashed line in Fig. 3a denotes the orientation of the data presented in Figs. 2 and 3. As can be seen, the data points are coded similarly to the corresponding 51.8 GHz data in Fig. 1.

As already discussed, the Hamiltonian for a well isolated effective spin \( S' = 1/2 \) Kramers’ doublet takes the form
\[
\hat{H} = \mu_{B} \vec{S}' \cdot \vec{g}' \cdot \vec{B},
\]
where \( \vec{g}' \) represents an effective Landé g-tensor that parameterizes all of the anisotropy associated with the spin-orbit coupling. The resulting relation between the measurement frequency, \( f \), and the resonance field, \( B_{\text{res}} \), is then \( h f = g(0) g B_{\text{res}} \). Thus, for a fixed frequency measurement, \( B_{\text{res}} = h f / g(0) B_{B} \). One can therefore attempt to fit the data in Fig. 3 assuming a simple angle dependence of the form \( g(\theta) = g_{\text{min}} + \delta g \cos^{2}(\theta - \theta_{o}) \), where \( g_{\text{min}} \) is the minimum \( g \)-value for a particular plane of rotation, \( \delta g \) is the difference between the minimum and maximum \( g \)-values, and \( \theta_{o} \) is the angle corresponding to \( g_{\text{min}} \). The magenta curves in Fig. 3 correspond to such fits. As can be seen, the agreement is quite good.

4. Conclusions

The orientations of the magnetic axes, with respect to the crystal lattice, were determined for single \( \text{Co}^{2+} \) ions doped into a nonmagnetic \( \text{Zn}_{4} \) complex. Frequency and temperature dependence studies confirm the ground state to be an effective spin \( S' = 1/2 \) Kramers’ doublet with a highly anisotropic \( g \)-factor. The anisotropy is found to be of the easy-axis type, with the single-ion easy axis directions tilted away from the crystallographic \( c \)-direction by \( 58^{\circ} \). The \( g \)-factor anisotropy \((g_{z} = 7.8 \text{ and } g_{x} \approx 2.0)\) is close to the maximum expected for an octahedral \( \text{Co}^{2+} \) complex \([19]\), suggesting a huge axial zero-field-splitting. It is presently unclear how the Kramers ions could combine into a \( \text{Co}_{4} \) complex to give rise to SMM behavior.

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Appendix A. Supplementary material

CCDC 627008 contains the supplementary crystallographic data for the compound referred in this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +(44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.11.018.

References


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\(^{1}\) For interpretation of references in color, the reader is referred to the web version of this article.