



Anisotropic exchange in a tetranuclear Co^{II} complex

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ABSTRACT

Very high-frequency (50–715 GHz) electron paramagnetic resonance (EPR) studies of the tetranuclear Co^{II} complex [Co(hmp)(dmb)Cl]₄ (**1**), where dmb is 3,3-dimethyl-1-butanol and hmp[−] is the monoanion of 2-hydroxy-methylpyridine, reveal the presence of significant zero-field-splitting (ZFS) within the ground state spin multiplet. Meanwhile, low-temperature hysteresis measurements of **1** (and related Co^{II} complexes) provide evidence for slow magnetization relaxation, suggesting that it could be a single-molecule magnet (SMM). However, EPR studies of a Zn analog of **1**, doped with a small quantity of Co^{II}, show the ground state of the Co^{II} ions to be an effective spin $S' = 1/2$ Kramers doublet with a highly anisotropic g -tensor. The question then arises as to the origin of the ZFS within the ground state spin multiplet of **1**, as well as the slow magnetization relaxation. Here, we consider the effect of anisotropic exchange interactions between the effective spin $S' = 1/2$ Kramers ions within the tetranuclear complex. Such exchange anisotropy arises naturally when one treats the ground state of high-spin Co^{II} as a Kramers doublet. Our model provides an explanation for the ZFS in the ground state observed via EPR, and can also account for qualitative features observed through magnetic measurements.

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1. Introduction

Research during the past two decades involving polynuclear transition metal clusters has resulted in the discovery of an exciting new class of molecular nanomagnets with fascinating quantum properties – so-called ‘single molecule magnets’ (SMMs [1]). SMMs derive their properties from a core of exchange-coupled transition metal ions such as Fe, Mn, and Ni. In many cases, the core comprises metal ions having multiple valence states [2–4] and, in some examples, mixed metal complexes have resulted in SMM behavior [4–6]. We note also that there now exist a few examples of SMMs involving rare-earth ions [7].

It is generally believed that the two most important ingredients for obtaining a good SMM are: (i) a large spin ground state, S ; and (ii) a significant negative (Ising-type) molecular anisotropy, D . When combined, these two ingredients can stabilize a sizeable energy barrier, $U \approx |D|S^2$, separating ‘up’ and ‘down’ spin projections. It is this barrier that results in magnetic bistability, and the possibility to magnetize a SMM at low-temperatures – hence the name. A large spin is best achieved by promoting ferromagnetic interac-

tions between the magnetic ions within a large cluster [8,9], though one can also attain large spin states in antiferromagnetic molecules where frustration can result in an uncompensated moment. The most obvious way to achieve a significant anisotropy is to work with metal ions that themselves are known to exhibit highly anisotropic single-ion properties, i.e. strong spin–orbit coupling [10].

With the above in mind, there have been several attempts to produce SMMs using Co^{II}, which is known to exhibit strong spin–orbit coupling in comparison to Mn^{II–IV}, Fe^{III} and Ni^{II}, from which the vast majority of known SMMs have been realized. The earliest report involved a Co₄ cluster very similar to the one that forms the basis for the present investigation [11]. In this study, magnetic hysteresis was observed below about 1 K, which was also weakly field-sweep-rate dependent – the classic signature of a SMM. Furthermore, magnetization measurements hinted at a sizeable spin ground state and a negative axial zero-field-splitting (ZFS) parameter, again suggesting that this Co₄ complex is a SMM. Since then, a few additional examples of homometallic polynuclear Co^{II} clusters have been reported which show signatures of SMM behavior [12–16]. However, no spectroscopic data have been reported in support of these assignments.

During the past few years, we have published extensive investigations of a family of tetranuclear Ni^{II} SMMs with the general formula [Ni(hmp)(ROH)X]₄, where hmp[−] is the anion of

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2-hydroxymethylpyridine, R is an alkyl substituent and X^- is either Cl^- or Br^- [4]. A key finding of this work was the fact that crystals of the high (S_4) symmetry $[Ni(hmp)(dmb)Cl]_4$ complex contained no solvate molecules, resulting in exceptionally high quality high-frequency electron paramagnetic resonance (HFEPFR) spectra [17]. Furthermore, HFEPFR measurements for a Zn analog doped with small quantities of Ni^{II} enabled evaluation of the single-ion ZFS tensors [18]. The combined studies provided important insights concerning the physics of SMMs [19]. The success of these investigations thus provided motivation for investigating two isostructural compounds: $[Co(hmp)(dmb)Cl]_4$ (**1**) and $[Zn_{1-x}Co_x(hmp)(dmb)Cl]_4$ (**2**).

Single-crystal HFEPFR studies of $[Zn_{1-x}Co_x(hmp)(dmb)Cl]_4$ were reported previously [20], demonstrating that the ground state of the Co^{II} ions can be modeled as an effective spin $S' = 1/2$ Kramers doublet. Such a model ignores the upper Kramers levels associated with the $S = 3/2$ Co^{II} ions. The strong anisotropy is instead parameterized via an anisotropic g -tensor associated with the effective $S' = 1/2$ ground state Kramers doublet. The HFEPFR studies of **2** established a huge g -anisotropy ($g_z = 7.8$ and $g_{x,y} \approx 2.0$) of the easy-axis type. It was also found that the individual easy-axis directions are tilted away from the crystallographic c direction by 58° . The huge g -anisotropy is close to the maximum expected for an octahedral Co^{II} complex [21], suggesting a very significant ZFS separating the two Kramers doublets. However, it was not possible to determine the magnitude of this ZFS on the basis of the HFEPFR studies of **2**.

The clear success in modeling the HFEPFR spectrum of the Co^{II} ions in crystals of complex **2** as effective spin-1/2 particles begs the obvious question as to whether such a simple approach may be extended to the polynuclear complex **1**. First and foremost, we note that a rigorous treatment of the spin-orbit coupling is computationally challenging (the Hamiltonian matrix has dimensions of 20736×20736), and also requires far more information concerning the Co^{II} ZFS than obtained from HFEPFR studies of **2**. Thus, in some sense, the coupled $S' = 1/2$ description offers the only realistic starting point. However, at first sight, it is not obvious how one could couple four $S' = 1/2$ particles, giving rise to SMM behavior. One associates the magnetic bistability of a SMM with the ZFS within its spin ground state. At a very basic level, this ZFS (or zero-field anisotropy) arises from the projection (or addition) of the ZFS associated with the individual ions onto the spin ground state of the molecule [9,22]. Herein lies the problem: a spin-1/2 object displays no anisotropy in the absence of a magnetic field, i.e. it exhibits no ZFS. Thus, such a projection by itself cannot give rise to ZFS for the coupled system. Viewed slightly differently – by ignoring the ZFS splitting associated with the Co^{II} ions, one is throwing away all details of their zero-field anisotropy.

The arguments given above ignore one crucial detail: in the case of the coupled Co_4 system, each Co^{II} ion experiences an exchange field due to its neighboring ions in the cluster. However, the projection method completely ignores this exchange coupling. The solution to this problem turns out to be relatively simple, and involves a multispin Hamiltonian consisting of just the pairwise interactions between the Co^{II} ions together with the individual Zeeman interactions. The anisotropic spin-spin interactions are then parameterized in terms of an exchange tensor, \vec{J}_{ij} , and the Hamiltonian may be expressed as:

$$H = \sum_{i < j} \hat{S}_i \cdot \vec{J}_{ij} \cdot \hat{S}_j + \sum_i \mu_B \vec{B} \cdot \vec{g}_i \cdot \hat{S}_i. \quad (1)$$

For the case of four coupled spin-1/2 particles, the full Hamiltonian matrix has dimensions $2^4 \times 2^4$, i.e. 16×16 . The problem is thus easily tractable, and involves just a handful of parameters, many of which are already known from the HFEPFR studies of complex **2** [20].

In this paper, we attempt to qualitatively account for the main features observed in the HFEPFR spectra obtained for the Co_4 complex **1** on the basis of Eq. (1), and we additionally consider the possibility that anisotropic exchange could give rise to magnetic bistability and SMM behavior. Naturally, the exchange anisotropy is merely a manifestation of the strong single-ion anisotropy associated with the individual Co^{II} ions. Nevertheless, this offers a new way of thinking about magnetic anisotropy in polynuclear clusters, and complex **1** appears to represent a model compound for exploring these ideas in detail.

2. Experimental

Crystals of complex **1** were prepared according to a similar procedure to the previously reported $[Co(hmp)(MeOH)Cl]_4$ complex [11]; a detailed account of the synthesis will be published elsewhere [23]. Good sized, dark red crystals form in the shape of a square-based pyramid, reflecting the S_4 symmetry of the structure. One can easily identify the principal crystallographic directions on the basis of the crystal morphology, the c -axis being oriented perpendicular to the square base of the pyramid, i.e. in the direction defined by the apex of the pyramid. All of the data presented in this paper were obtained with the magnetic field applied parallel to the crystal c -axis, which also corresponds to the S_4 axis; angle-dependent studies will be published in a longer paper. The sample was mounted with its square base attached with vacuum grease to a flat copper disk at the end of the HFEPFR probe/cavity.

Experiments were performed in a 9 T superconducting magnet, and temperature control achieved using a 4He flow cryostat equipped with a calibrated temperature sensor. As a spectrometer, we utilized a Millimeter-wave Vector Network Analyzer (MVNA, described elsewhere [24,25]), enabling measurements from 8 to 715 GHz at the University of Florida. At the higher frequencies (>200 GHz), a pair of external Gunn diodes were associated with the MVNA on both source and detection sides, enabling phase sensitive measurements up to 715 GHz. A quasioptical spectrometer was used for frequencies above ~ 200 GHz. This spectrometer, which has been described previously [26], employs a tapered corrugated HE_{11} waveguide tube, enabling single-pass reflectivity measurements with good coupling to relatively small crystals ($< 1 \text{ mm}^3$). For frequencies below 200 GHz, a cavity perturbation technique was employed (see [24,25]).

3. Data and discussion

Fig. 1 shows low-temperature ($T = 2 \text{ K}$) HFEPFR spectra obtained at several frequencies in the range from 258 to 715 GHz. Multiple peaks are observed at all frequencies. The signal-to-noise diminishes at the higher frequencies due to the reduced dynamic range of the high-frequency spectrometer. Nevertheless, clear resonances are observable at all of the frequencies shown, and each spectrum is highly reproducible. Given that the temperature is rather low (much less than the microwave quantum, which ranges from 12 to 34 K), one may assume that all of the observed HFEPFR intensity involves excitations from the ground state of the Co_4 complex. Several obvious resonance branches become apparent upon close inspection of Fig. 1; this point has been emphasized by means of the colored arrows in the figure.

A 2D frequency versus field plot for resonances observed at many different frequencies, spanning a wider range from 50 to 715 GHz, is displayed in Fig. 2. This figure emphasizes only the stronger resonances, particularly those observed at the lowest temperatures (though data points are included for a range of temperatures). The solid curves superimposed on the various resonance branches are simply guides to the eye. The first point to

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