Magnetism of a novel tetranuclear nickel(II) cluster in strong magnetic fields

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Abstract. High frequency Electron Spin Resonance (ESR) up to $\nu = 1$ THz and magnetization $M(B)$ of a tetranuclear-Ni(II) single molecular complex of type $[L_2Ni_4(N_3)(O_2CAda)_4](ClO_4)$ featuring an unprecedented central $\mu_4$-1,1,3,3 azide have been studied in magnetic fields up to $B = 55$ T. Bridging ligands provide intramolecular exchange paths of different strength between the four Ni ions each having a spin $S_{Ni} = 1$. T- and $\nu$-dependent ESR measurements enable to accurately determine the energy spectrum of the spin states of the cluster as a function of $B$. A predominantly antiferromagnetic character of exchange renders the ground state nonmagnetic, $S = 0$, with a number of excited magnetic multiplet states, $S = 1, \ldots, 4$. Remarkably, ESR gives evidence for the spin-level crossing in a field of $\sim 25$ T which turns the ground state of the cluster to a strongly magnetic one. This observation is confirmed by the static $M(B)$ data.

1. Introduction

An important objective of the synthesis of single molecule magnets is the design of molecular complexes with a large spin multiplicity and a strong magnetic anisotropy. Regarding the latter issue nickel(II) is increasingly used because it often shows a significant single ion anisotropy \cite{1, 2}. Recently a novel class of tetranuclear Ni(II) complexes that feature a genuine $\mu_4$-1,1,3,3 azide coordination has been communicated \cite{3}. Owing to the complexity of the spectrum of the spin states arising from the exchange coupling within a molecule a comprehensive understanding of the magnetism requires application of both bulk and local magnetic probes such as magnetization and electron spin resonance. In particular, tunable sub-Terahertz-ESR spectroscopy in strong magnetic fields turned out to be essential for an accurate characterization of the ground state properties and low-lying magnetic excitations of the tetranuclear Ni-Azide complex \cite{4}.

In this paper high-field ESR and static magnetization results on a quadruple-Ni(II) complex of type $[L_2Ni_4(N_3)(O_2CAda)_4](ClO_4)$ are presented. The data reveal a non-magnetic ground state of the complex which turns into a magnetic one in strong magnetic fields above $B_{crit} \sim 25$ T due to a spin-level crossing. A significant magnetic anisotropy gap amounting to $\sim 7$ K in the first...
excited spin multiplet $S = 1$ has been observed. A semi-quantitative analysis in the framework of a minimal effective spin Hamiltonian yields a good description of the experimental data.

2. Experimental
The studied Ni(II)-complex which molecular structure is shown in figure 1a has been synthesized and characterized according to Ref. [3]. Powder samples pressed in a pellet have been investigated. ESR in static fields up to 15 T was measured with a Millimeterwave Vector Network Analyzer from AB Millimétré and in pulsed fields up to 40 T with a setup employing a Fabry-Perot cavity optically pumped by a CO$_2$ laser. The magnetization $M(B,T)$ up to 5 T was measured with a SQUID magnetometer from Quantum Design and in pulsed magnetic fields up to 55 T by an inductive technique with a system comprising two concentric pick-up coils in opposition to each other and additional compensation coils.

3. ESR results and analysis
ESR was studied at frequencies 0.1-1 THz. The spectrum at elevated temperatures consists of four resonance modes which at a constant frequency $\nu$ occur at different resonance fields $B_{i}^{\text{res}}$. The respective $\nu$ vs. $B_{i}^{\text{res}}$-relations (resonance branches) together with the representative spectra are shown in figure 2. Extrapolation of the $\nu(B_{i}^{\text{res}})$-dependences to zero field reveals a finite energy gap $\Delta_{1} = 139$ GHz (6.7 K) for branches 1 and 2 and no gap for branches 3 and 4.

At $\nu < 1$ THz the intensities of the modes $I_{i}(T)$ follow a thermal activation behavior (figure 3a). Their sum $\sum_{i} I_{i}$ shows a $T$-dependence similar to the static susceptibility $\chi = M/B$ (figure 3b). This gives evidence that ESR probes the same Ni-spins which determine the static magnetic response. A strong decrease of $I_{i}(T)$ and $\chi(T)$ at low $T$ indicates a non-magnetic ground state of the Ni(II)-complex. Remarkably, resonances 1, 2 and 4 follow a common $T$-behavior with maxima at $\sim 30$ K, whereas resonance 3 has a broad maximum at $\sim 150$ K. One can assign therefore peaks 1, 2 and 4 to the first excited magnetic state and peak 3 to the second excited state of the complex. From the slopes of the $\nu(B_{i}^{\text{res}})$-dependences at high fields one can derive the $g$ factors. The values are typical for Ni(II) and amount to 2.11, 2.18 and 2.08 for branches 2, 3 and 4 respectively. A much stronger slope of branch 1 indicates that it results from a ‘forbidden’ spin-flip transition (see below).

An important new feature appears in the ESR spectrum measured at $\nu = 1.017$ THz. A strong
and broad absorption signal arises at \( B > 25 \text{T} \). It can be identified with resonance 2 (figure 2). Noteworthy the signal is seen at 4.2 K and vanishes above 10 K that allows to identify resonance 2 in the high-field regime with the ground state excitation. At still higher temperatures a thermally activated signal assigned to branch 3 develops in the spectrum (figure 2).

To analyze the experimental data we introduce a minimal effective Hamiltonian in the form

\[
\mathcal{H} = J_1 (\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_3 \cdot \mathbf{S}_4) + J_2 (\mathbf{S}_1 \cdot \mathbf{S}_3 + \mathbf{S}_2 \cdot \mathbf{S}_4) + J_3 (\mathbf{S}_1 \cdot \mathbf{S}_4 + \mathbf{S}_2 \cdot \mathbf{S}_3) + D \sum_{i=1,4} [S_{2iz}^2 - S_{Ni}(S_{Ni} + 1)/3] + g\mu_B \vec{B} \cdot \sum_{i=1,4} \vec{S}_i
\]

Here, term (1) represents the isotropic intramolecular magnetic coupling between the Ni spins \( \vec{S}_i \) which assumes three exchange paths described by the exchange couplings \( J_{1,2,3} \) (figure 1). Term (2) describes the single-ion anisotropy of the Ni(II) ions arising due to the influence of the anisotropic ligand crystal field (CF) and the spin-orbit coupling. This anisotropy yields a splitting of the spin states of a Ni ion in zero magnetic field (so-called zero field gap) which magnitude is proportional to the anisotropy parameter \( D \). Term (3) is the Zeeman interaction with the external field \( \vec{B} \). Here, \( g \) is the Ni(II) \( g \) factor. In this model the much weaker intermolecular interactions are neglected.

Since in the powder ESR spectrum the most spectral weight is caused by the microcrystallites having their CF anisotropy axis \( \vec{c} \) close to the perpendicular direction to the magnetic field it is appropriate to consider the energy spectrum of the spin states for the case \( \vec{c} \perp \vec{B} \). Details of the combined analysis of the \( \chi(T) \) (figure 3a) and ESR data (figure 2) in the framework of the above Hamiltonian can be found in Ref. [4]. Here we summarize the main results. The following hierarchy of the coupling parameters has been found: \( J_1 = 37.3 \text{K} \) (antiferromagnetic (AF)

![Figure 3](image-url)  
**Figure 3.** (a) \( T \)-dependence of the intensities \( I_i \) of the resonance modes and of their sum \( \sum_i I_i \) and \( \chi(T) = M(T)/B \) and \( \chi(T)T \) at \( B = 0.5 \text{T} \). Curie-like tail below 20K is due to \( \sim 2\% \) of impurities. Solid lines are data fits (see the text).

![Figure 4](image-url)  
**Figure 4.** (a) Energy diagram of the low lying spin levels. Note the level crossing at \( B_{\text{crit}} \sim 25 \text{T} \). (b) \( M(B) \)-dependence at \( T = 1.45 \text{K} \) and 4.2 K. Note a step-like increase of \( M(B) \) around \( B_{\text{crit}} \). Dot lines indicate a linear background at low- and high fields (see the text).
coupling), $J_2 = -57.8 \, \text{K}$ (ferromagnetic (FM)) and a diagonal exchange $J_3 = 37.1 \, \text{K}$ (AF). The respective coupling scheme is shown in figure 1b where pairs of FM coupled ions (1,3) and (2,4) interacting AF through $J_1$ and $J_2$ are depicted. The energy gap $\Delta_1 = 6.7 \, \text{K}$ observed for branches 1 and 2 can be related to the Ni(II) single ion anisotropy yielding the parameter $D = -0.72 \, \Delta_1 = -4.8 \, \text{K}$. The numerical solution of the Hamiltonian with the above parameters yields the following three low-energy multiplets of the tetranuclear Ni(II)-complex: A nonmagnetic singlet ground state, $S = 0$, the first excited triplet state, $S = 1$, at the energy $E_{0,1} \simeq 37 \, \text{K}$ and the second excited quintuplet state, $S = 2$, at the energy $E_{0,2} \simeq 3 \, E_{0,1}$ (figure 4). The remaining $S = 3$ and $S = 4$ multiplets lie at even higher energies and are not considered for simplicity.

ESR branches 1, 2 and 4 can be straightforwardly assigned to the excitations within the $S = 1$ multiplet. Branch 1 showing the zero field gap $\Delta_1$ is a so-called 'forbidden' transition between levels labelled as $| - \rangle$ and $| + \rangle$ in figure 4a which in small magnetic fields are the mixture of $| -1 \rangle$ and $| +1 \rangle$ spin states due to the CF effect and the spin-orbit coupling. Branch 2 showing the same gap is the transition between $| 0 \rangle$ and $| - \rangle$ states. The gapless branch 4 is the transition between $| 0 \rangle$ and $| + \rangle$ states. From the analysis of the $I_i(T)$-dependences branch 3 has been ascribed to the transitions within the second excited $S = 2$ multiplet. Since the zero field splitting in this multiplet is almost absent (figure 4a) individual transitions $| - - \rangle \leftrightarrow | - \rangle$, $| - \rangle \leftrightarrow | 0 \rangle$, $| 0 \rangle \leftrightarrow | + \rangle$ and $| + \rangle \leftrightarrow | ++ \rangle$ occur at practically the same resonance field and contribute therefore to the same line.

4. Spin level crossing in strong magnetic fields

The calculated field dependence of the spin state energies suggests the change of the ground state to a magnetic one at $B > B_{\text{crit}} \sim 25 \, \text{T}$ owing to the crossing of the $| -1 \rangle$ level of the $S = 1$ multiplet with the $S = 0$ singlet at $B_{\text{crit}}$ (figure 4a). The ESR data at $\nu = 1.017 \, \text{THz}$ give strong experimental evidence for the spin level crossing. At this frequency the resonance field of peak 2 exceeds $B_{\text{crit}}$. Therefore the excitation from the $| -1 \rangle$ to the $| 0 \rangle$ level becomes a ground state excitation which explains the observation of resonance 2 at a low temperature of $4.2 \, \text{K}$.

An additional confirmation of the spin level crossing comes from the low temperature $M(B)$ data in pulsed magnetic fields (figure 4b). A broad step-like increase of the magnetization around $25 \, \text{T}$ clearly indicates the change of the ground state related to the level crossing at $B_{\text{crit}}$. Remarkably, one finds an appreciable increase of $M$ even at small fields $B \ll B_{\text{crit}}$ which gets even stronger in the high field regime. Such additional contribution to $M$ suggests a substantial admixture of the $S = 1$ multiplet to the ground state singlet $S = 0$ which may occur in the presence of the anisotropic Dzyaloshinsky-Moriya (DM) interaction, as has been recently theoretically modelled in Ref. [5].

5. Conclusions

High-field ESR and magnetization studies of a novel tetranuclear Ni(II)-complex with a central azide bridge yield a detailed characterization of the low energy spectrum of the spin states. Experimental data provide compelling evidence for the tuning of the ground state of the complex by application of a strong magnetic field.

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