Origin of the fast magnetization tunneling in tetranuclear nickel single-molecule magnets

David N. Hendrickson a,*, En-Che Yang a, Rose Marie Isidro a, Cem Kirman b, Jon Lawrence b, Rachel S. Edwards b, Stephen Hill b,*, Akira Yamaguchi c, Hidehiko Ishimoto c, Wolfgang Wernsdorfer d, Chris Ramsey e, Naresh Dalal e, Marilyn M. Olmstead f

a Department of Chemistry and Biochemistry-0358, University of California at San Diego, La Jolla, CA 92093-0358, USA
b Department of Physics, University of Florida, Gainesville, FL 32611, USA
c Institute of Solid State Physics, The University of Tokyo, Kashiwanoha 5-1-5, Kashiwa, Chiba 277-8581, Japan
d Laboratoire Louis Néel-CNRS, 25 Avenue des Martyrs, 38042 Grenoble Cedex 9, France
e Department of Chemistry, Florida State University, Tallahassee, FL 32306, USA
f Department of Chemistry, One Shields Avenue, University of California at Davis, Davis, CA 95616, USA

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Abstract

Several tetranuclear nickel(II) single-molecule magnets (SMMs) have been prepared with the general composition of \([\text{Ni(hmp)-(ROH)}X]_4 \rightarrow \text{S}\), where \text{hmp} is the monoanion of 2-hydroxymethylpyridine, \(X\) is either \(\text{Cl}\) or \(\text{Br}\) and \(\text{S}\) is the solvate molecule. Magnetization versus magnetic field hysteresis loops for these \(\text{Ni}_4\) SMMs show that there is a relatively fast rate of magnetization tunneling (small coercive field) and, in certain cases, an exchange bias present. Detailed measurements have been carried out in order to determine the origin of the fast magnetization tunneling. High-field electron paramagnetic resonance (HFEPR) data were collected on a single crystal of \([\text{Zn(hmp)}(\text{dmb})\text{Cl}]_4\) doped with a small amount of \(\text{Ni(II)}\), where, \(\text{dmb}\) is 3,3-dimethyl-1-butanol. These variable-frequency/temperature data give values of the single-ion zero-field splitting parameters \(D_i\) and \(E_i\), and the orientations of these interactions, for the single \(\text{Ni}^{II}\) ions in a \(\text{Zn}_3\text{Ni}\) complex doped into a \(\text{Zn}_4\) crystal. HFEPR data were also obtained at many frequencies and temperatures for a single crystal of isostructural \([\text{Ni(hmp)}(\text{dmb})\text{Cl}]_4\). Rotation of the single crystal such that the external field is positioned in the hard plane clearly establishes that the transverse zero-field interaction \(B_{ij}^4\) is the cause of the fast magnetization tunneling in the \(S = 4\) ground state of this SMM. The magnitude of \(B_{ij}^4\) and the \(\text{Ni}_4\) \(D\) value can be related to the directionality and magnitude of the \(D_i\) and \(E_i\) interactions at the individual \(\text{Ni}^{II}\) ions, determined for the doped crystal. The microenvironments and ligand dynamics were probed by means of a single-crystal X-ray structure at 12 K and by heat capacity data.

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1. Introduction

Polynuclear metal complexes with high spin ground states and significant negative magnetoanisotropy have attracted considerable attention. Such molecules show magnetic hysteresis and quantum tunneling of magnetization (QTM), and are called single-molecule magnets (SMMs) [1–3]. In particular, transition metal complexes with the cubane structure have been extensively studied; for example, many tetra-nickel(II) (\(\text{Ni}_4\text{O}_4\)) cubane metal cluster are known to be ferromagnetically coupled to give a \(S = 4\) ground state.

* Corresponding author. Tel.: +1 858 534 6085; fax: +1 858 534 5383.
E-mail addresses: dhendrickson@ucsd.edu (D.N. Hendrickson), enyang@ucsd.edu (E.-C. Yang).

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The origin of the exchange interactions in such compounds has been studied and correlated to the Ni–O–Ni angle within the cubane [6]. In addition to the high spin number, many tetra-nickel cubane molecules also have high molecular symmetry. These characteristics make such molecules great candidates for detailed studies of the origin of zero-field splitting (zfs) and the mechanism for fast magnetization relaxation [7].

Recently, we found a series of Ni4 cubane metal complexes, with hmp− (mono-anion of 2-hydroxymethylpyridine) as the bridging ligand, having four-fold pseudo rotation (S4) symmetry [8,9]. Here, we present data for this series of Ni4 SMMs. Preliminary results of micro-SQUID magnetometry and high-frequency electron paramagnetic resonance (HFEPR) measurements on single crystals are presented to characterize these Ni4 SMMs. Fast tunneling of the magnetization is observed in the hysteresis loops. To explore the reasons for the fast tunneling, as well as the origin of the zfs of the molecule, we set out to determine the zfs parameters of the individual NiII ions by doping small amounts of NiII into a Zn4 cubane molecule matrix. Due to the observation of splitting of the peaks in the HFEPR spectra of one of these Ni4 cubane complexes, heat capacity measurements and low temperature X-ray diffraction studies were also carried out to probe the possible cause of the splitting features.

2. Experimental

2.1. Syntheses

Crystalline samples of complexes 1, 2, and 3 ([Ni(hmp)−(ROH)Cl]4, R = methyl for 1, ethyl for 2, 3,3-dimethyl-1-butyl for 3) were prepared as previously reported [8,9].

2.2. Physical measurements

High frequency (40–200 GHz) single crystal EPR measurements were carried out using a millimeter-wave vector network analyzer and a high sensitivity cavity perturbation technique; this instrumentation is described elsewhere [10]. Tunneling studies were performed by magnetization measurements on a single crystal using an array of micro-SQUIDs as described in the literature [11]. Specific heat at constant pressure (Cp) measurements at zero-field were made using a quantum design physical properties measurement system (QD PPMS) employing a relaxation method [12]. The platform was calibrated by use of a copper standard.

3. Results and discussion

3.1. Description of structures

In this paper, data are presented for the series of [Ni(hmp)(ROH)Cl]4 complexes, where R stands for the Me, Et, or 3,3-dimethyl-1-butyl groups. An example drawing of the structure of the Ni4 cubane molecule is shown in Fig. 1. The common feature of the structure of the Ni4 cubane molecule is that the molecular core consists of four NiII cations occupying the alternating corners of a distorted cube with oxygen atoms on the other four corners. The four NiII (S = 1) ions ferromagnetically couple through the bridging oxygen atoms to give a S = 4 ground state. The structure of the Ni4 cube is such that the molecule has S4 site symmetry. As in the case for Mn12, this four-fold symmetry can impose a uniaxial zfs D term, while the transverse E term should be equal to zero on symmetry grounds [13].

3.2. Magnetization hysteresis loops

Previously, we reported [8,9] that this series of complexes shows magnetization hysteresis loops. When the R groups on the alcoholic ligand are small, such as methyl or ethyl, weak intermolecular magnetic exchange interactions are present, leading to an exchange bias of the hysteresis loops, where the first step feature in the loops is significantly shifted from zero field. However, the intermolecular interactions can be turned off by introducing a more bulky aliphatic chain on the alcoholic ligands. Fig. 2 shows the magnetization hysteresis loop for complex 3. It can be seen that the first magnetization tunneling step occurs essentially at zero field. Another important feature to note is that the rate of this quantum tunneling is very fast compared to other known SMMs such as the Mn12 and Mn4 complexes.

Fig. 1. ORTEP representation of [Ni(hmp)(MeOH)Cl]4 showing 50% probability ellipsoids.
To explore the origin of this fast tunneling, a series of HF EPR experiments were performed on complex 3.

3.3. High-frequency EPR data for the Ni₄ cubane molecule

Single-crystal HF EPR data were collected for complex 3. The results of a preliminary analysis of these data reveal that these Ni₄ complexes have a \( S = 4 \) ground state and that the axial zero-field splitting parameter \( D \) is negative [8,9]. Due to the molecular \( S_4 \) symmetry, it is required that the rhombic zfs \( E \) term be zero. Therefore, the fast tunneling of magnetization can be the result of fourth order transverse zero-field interactions, namely the \( B_4^4 \) term [14]. The final effective spin Hamiltonian will thus be:

\[
\hat{H} = g_\nu \mu_B \mathbf{B}_z \cdot \mathbf{S}_z + D S_z^2 + B_4^0 \hat{O}_4^0 + B_4^4 \hat{O}_4^4. \tag{1}
\]

The HF EPR spectra confirm the absence of the \( E \) term and a significant \( B_4^0 \) term for the molecule. In addition to the discovery of a large \( B_4^4 \) term, some interesting features have also been observed in the low temperature HF EPR spectra. Fig. 3 presents a few low temperature spectra. As the temperature is reduced from 60 to 30 K, fine structure resonances are observed to split into two features. The low temperature (12 K) X-ray structure confirmed that there are disordered ligand carbon atoms. It is likely that there is a dynamic ligand conformation at high temperatures that becomes frozen into a static disorder below about 50 K.

3.4. Heat capacity measurements

To find the origin of the HF EPR peak splitting observed for Ni₄ cubane complex 3 that occurs around 45 K, heat capacity measurements were performed on complex 3 in the temperature range 2–100 K. It can be seen from Fig. 4 that a peak shows up in the heat-capacity versus temperature plot. This peak indicates there is an order–disorder phase transition at 47 K. The fact that the peak in heat capacity occurs at the same temperature as the peak splitting in the HF EPR spectra further confirms that it is due to a static ligand disorder. Further analysis of the heat capacity data is in progress.

3.5. HF EPR of Niᴵᴵ doped [Zn(hmp)(dmb)Cl]₄ complex

Single-crystal data were collected to determine the zfs parameters of individual Niᴵᴵ ions in the cubane metal cluster. With the knowledge of the single-ion zfs parameters we may understand the fast tunneling, and the relationship between single-ion and molecular zfs parameters. We have chosen an analog of complex 3,

![Magnetization (M) of a single crystal of [Ni(hmp)(dmb)Cl]₄ (plotted as a fraction of the maximum value of \( M_s \), the saturation magnetization) versus applied magnetic field (\( \mu_0 H \)). The magnetic field is parallel to the easy axis. The magnetization loops were obtained at 0.040 K at two different scan rates.](image1)

![Variable temperature HFEPR spectra obtained at 172 GHz for a single crystal of [Ni(hmp)(dmb)Cl]₄. The magnetic field is oriented parallel to the easy axis of magnetization of the crystal.](image2)

![Heat capacity at constant pressure versus temperature for a polycrystalline sample of complex 3.](image3)
the NiII doped Zn4 cubane molecule, as the candidate to study the zfs of individual NiII ions. The fact that there is only one symmetry independent molecule in the crystal lattice makes it easier to interpret the spectra. Furthermore, complex 3 contains no solvent in its structure, which could distort the EPR spectra.

The zfs parameters of the individual NiII ion were found by rotating the applied magnetic field about different crystallographic planes. Fig. 5 illustrates some of the angle-dependent HFEPR spectra obtained at 120 GHz for a single crystal of a NiII doped [Zn(hmp)(dmb)Cl]4 sample.

![Graph](image)

Fig. 5. Angle-dependent HFEPR spectra obtained at 120 GHz for a single crystal of a NiII doped [Zn(hmp)(dmb)Cl]4 sample.

4. Conclusion

A series of molecules with the composition [Ni(hmp)-(ROH)Cl]4, where R = CH3 for complex 1, R = Et for complex 2 and R = 3,3-dimethyl-1-butyl for complex 3, have been shown to be SMMs. Complex 3 shows no exchange bias in its magnetization hysteresis loop, with a clear step feature at zero magnetic field. The fast QTM process in complex 3 is likely the result of a significant B4 term, and the tilting of the single NiII ion zfs tensor. Small structure changes cause the splitting of the HFEPR fine-structure resonances as confirmed by heat capacity data.

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References