# High-frequency electron paramagnetic resonance investigations of tetranuclear nickel-based single-molecule magnets

R. S. Edwards[a)] and S. Maccagnano
*Department of Physics, University of Florida, Gainesville, Florida 32611*

E.-C. Yang
*Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, California 92093*

S. Hill
*Department of Physics, University of Florida, Gainesville, Florida 32611*

W. Wernsdorfer
*Laboratoire Louis Néel-CNRS, 25 Avenue des Martyrs, 38042 Grenoble Cedex 9, France*

D. Hendrickson
*Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, California 92093*

G. Christou
*Department of Chemistry, University of Florida, Gainesville, Florida 32611*

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We report preliminary high-frequency electron paramagnetic resonance (EPR) investigations for several tetranuclear nickel complexes which exhibit single-molecule magnetism, including low-temperature (below $\sim 1$ K) hysteresis loops and resonant magnetic quantum tunneling. The combination of a cavity perturbation technique and a split-coil magnet facilitates high-sensitivity, multifrequency (40 to 200+ GHz), angle dependent single-crystal EPR measurements. The data confirm the expected $S=4$ ground states, and a negative magnetocrystalline anisotropy for each member in the series. An unusual splitting of the easy-axis EPR peaks is observed, which may be interpreted in terms of distinct $Ni_4$ species within the crystals. Overall, however, the trends associated with the splitting, as well as the EPR linewidths and shapes, suggest that intermolecular exchange interactions are important. Indeed, differences between the EPR spectra obtained for different complexes correlate nicely with the expected strength of exchange interactions, as determined both from intermolecular contact distances and from independent hysteresis measurements. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1540050]

## I. INTRODUCTION

Single-molecule magnets (SMM's) have recently become the subject of extensive investigation. Their main attraction is an intrinsic bistability which is realized via a large spin ground state and a significant negative (easy-axis) magnetocrystalline anisotropy.[1] This bistability has aroused great interest in terms of the use of SMM's in future molecular devices. When grown as crystals, the magnetic unit is monodisperse—each molecule in the crystal has the same spin, orientation, magnetic anisotropy, and atomic structure. Thus, SMM's enable fundamental studies of properties intrinsic to magnetic nanostructures that have previously been inaccessible. For example, recent studies of SMM's have revealed the quantum nature of the spin dynamics in a nanomagnet,[1,2] i.e., quantum tunneling of a large magnetic moment from "up" to "down." An ability to tunnel coherently raises the prospect of manipulating entangled states of SMM's for quantum computation.

We have recently synthesized a series of SMM's based on tetranuclear nickel clusters with varying ligands, e.g., the complexes $[Ni(hmp)(MeOH)Cl]_4$, $[Ni(hmp)(EtOH)Cl]_4$, and $[Ni(hmp)(tBuEtOH)Cl]_4$, which we call MeOH, EtOH and tBuEtOH for short. Each complex has been predicted to have a spin $S=4$ ground state, and an easy-axis type anisotropy. Recent low-temperature ($<1$ K) hysteresis experiments have shown that the magnetic moments associated with each of these SMM's *do* exhibit resonant magnetic quantum tunneling (MQT).[3] However, in the first two complexes, the expected zero-field MQT resonance is shifted considerably away from $B=0$; this behavior may be attributed to an appreciable intermolecular exchange bias effect which was recently reported for a dimer system of manganese SMM's.[2,4]

The existence of significant inter-SMM exchange interactions in these nickel-based SMM's is not unexpected since
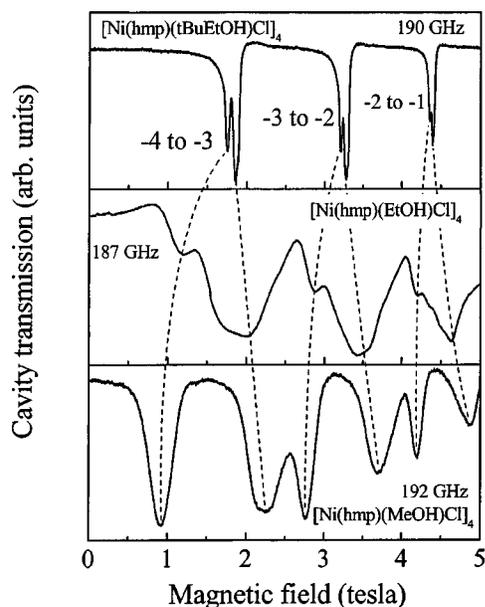
[a)]Electronic mail: edwards@phys.ufl.edu

FIG. 1. Raw EPR spectra for three different $Ni_4$ SMM's, obtained with the field approximately aligned with the easy axes; the temperature and frequencies are indicated. In the top panel, the resonances are labeled according to the $M_S$ quantum numbers involved in the transitions. Each peak shows a splitting which increases from top to bottom; the dashed lines indicate how the peaks evolve from one complex to the next.
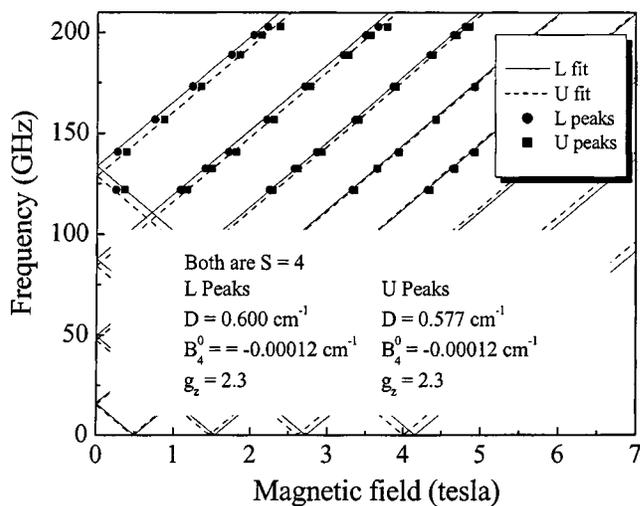


FIG. 2. Separate fits to Eq. (1) for the lower (L) and upper (U) peaks within each split doublet for the tBuEtOH complex. These fits confirm the $S=4$ ground state and yield diagonal components of the effective spin Hamiltonian. Similar fits (not shown) were obtained for the EtOH and MeOH complexes.

the intermolecular Cl–Cl contact distances are rather short ($\sim$4.8 to 6 Å). Through systematic variations of the ligands, it is possible to tune these exchange effects, e.g., by varying the Cl–Cl contact distance from $\sim$4.9 Å in the MeOH and EtOH complexes, to $\sim$6 Å in the tBuEtOH complex. In this study, we characterize the effects of inter-SMM exchange interactions through the use of high-frequency electron paramagnetic resonance (EPR).

The effective spin Hamiltonian for an isolated SMM is[1]

$$\hat{H}_i = D\hat{S}_{zi}^2 + E(\hat{S}_{xi}^2 - \hat{S}_{yi}^2) + g\mu_B \mathbf{B} \cdot \mathbf{S}_i + \hat{O}_4 + \hat{H}_i' ; \quad (1)$$

where $\mathbf{S}_i$ is the single spin operator with components $\hat{S}_{xi}$, $\hat{S}_{yi}$, and $\hat{S}_{zi}$; $D$ is the uniaxial anisotropy constant and $E$ characterizes the transverse anisotropy in the plane perpendicular to the easy axis; $g$ is the Landé $g$ factor and $\mathbf{B}$ is the applied field; $\hat{O}_4$ denotes weak fourth-order crystal field terms and $\hat{H}_i'$ describes additional perturbations that take into account disorder, exchange effects and intermolecular dipolar interactions.[2,4–6] While the Hamiltonian which includes exchange interactions within a dimer system is relatively simple to write down,[2,4] the case here is not straightforward since one should consider the exchange (of unknown sign) between several discrete near neighbors.

## II. RESULTS AND DISCUSSION

High-frequency (40 to 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.[7] Temperature control in the range from 2 to 80 K was achieved using a variable-flow cryostat. The magnetic field

was provided by a superconducting split-pair magnet, which enables angle dependent studies and approximate alignment of the single crystals.[6,7]

Figure 1 shows raw field sweeps for each of the three complexes; in each case, the field is roughly aligned with the easy axis, the frequency is approximately 190 GHz, and the temperature is 10 K. Data obtained for the tBuEtOH complex are the easiest to interpret. A series of more-or-less evenly spaced double peaks is observed, with the intensity decreasing for successive pairs of peaks. One possible interpretation for the splitting involves the existence of two species of molecules within the crystal, with slightly different crystal field parameters. Separate fits to the $S=4$ Hamiltonian [Eq. (1)] for the lower (L) and upper (U) split peaks are shown in Fig. 2. Although the fits are excellent, such an interpretation is inconsistent with x-ray studies which indicate that all molecules are crystallographically identical (with $S4$ site symmetry) and that no disorder associated with the ligands exists. Careful angle dependent studies rule out crystal twinning or sample misalignment as a possible explanation for the splitting.

EPR spectra for the EtOH and MeOH complexes reveal considerably broader absorptions and dramatically enhanced splittings. Assignments of the peaks were determined from their temperature dependence (not shown), and from similar fits to the one shown in Fig. 2 for the tBuEtOH complex. The evolution of the peaks for the three complexes are indicated in Fig. 1 by dashed lines, and assignments in terms of the $M_S$ quantum numbers are given in the top panel. In every case, fits to the $S=4$ Hamiltonian for the L and U peaks are surprisingly good (not shown), yielding the following parameters: $D_L = -0.715$ cm$^{-1}$, $D_U = -0.499$ cm$^{-1}$, $B_4^0 = -2 \times 10^{-4}$ cm$^{-1}$ and $g_z = 2.24$ for the MeOH complex, and $D_L = -0.673$ cm$^{-1}$, $D_U = -0.609$ cm$^{-1}$, $B_4^0 = -1.2 \times 10^{-4}$ cm$^{-1}$ and $g_z = 2.20$ for the EtOH complex. $E$ values ($\approx D/10$) have been determined from powder spectra and will not be discussed here.

While an explanation for the EPR splittings in terms of crystallographically distinct $Ni_4$ species cannot be ruled out in the case of the EtOH and MeOH complexes (their structures are each composed of two interpenetrating diamond lattices), it is interesting to note that the magnitudes of the splittings scale roughly with the expected strength of the exchange interactions, as determined both from the Cl–Cl contact distances and from the relative magnitudes of the exchange bias effects observed from hysteresis experiments; the MeOH complex shows an appreciably larger exchange bias effect than the EtOH complex, while the tBuEtOH complex shows no measurable exchange bias.[3] The EPR linewidths and shapes are also considerably broader and more complex for the two SMM's that show a clear exchange bias effect. We note that EPR line broadening due to intermolecular exchange interactions is well documented in other SMM's,[5,6] and EPR line splittings may also be expected on the basis of a simple dimer model which includes the effects of exchange between pairs of SMM's.[2,4] Explanations involving distinct crystallographic species are not consistent with all of our data, particularly in the case of the tBuEtOH complex. Clearly, therefore, a more detailed model which includes intermolecular exchange interactions between near neighbors is required in order to fully understand these EPR spectra.

## III. CONCLUSION

In summary, we report preliminary high-frequency single-crystal EPR measurements for a series of tetranuclear nickel SMM's. The data confirm the expected $S = 4$ ground states, and the negative magnetocrystalline anisotropy ($D < 0$) for each member in the series. An unusual splitting of the EPR peaks may, in some cases, be interpreted in terms distinct $Ni_4$ species within the crystals. However, the overall trends associated with the splittings, as well as the EPR linewidths and shapes, seem to be consistent with increasing intermolecular exchange interactions as one goes from the weakly interacting tBuEtOH complex to the strongly exchanging MeOH complex. This family of SMM's provides unique opportunities to systematically control and subsequently investigate many body interactions and environmental couplings between nanomagnets, and further modifications to these complexes are under investigation. Finally, we note that single crystal measurements are essential for this type of study, and further work is in progress.

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