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A cubane-type nickel single-molecule magnet with exchange-biased quantum tunneling of magnetization

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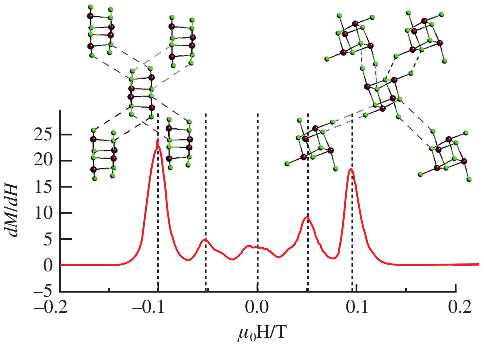
Low temperature magnetization measurements were performed on single crystals of the pyridyl-alcohol-supported [Ni(μ_3-Cl)Cl(HL·S)]$_4$ coordination cluster and they revealed open hysteresis loops up to 30 mK at a sweep rate of 0.07 T s^{-1}. The studied molecule with intramolecular ferromagnetic coupling J_{intra} of 15.251 K (+10.6 cm^{-1}) is an exchange-biased single-molecule magnet that exhibits intermolecular antiferromagnetic coupling J_{inter} of –0.004 K (–0.003 cm^{-1}) in the supramolecular environment of four other cubane-type units. Quantum tunneling of magnetization characterized by five steps at –0.1, –0.05, 0, 0.05 and 0.1 T was observed.



Keywords: nickel, tetranuclear metal complex, single-crystal measurements, magnetism, intermolecular exchange coupling.

The field of molecular spintronics[1] has been shown to benefit from supramolecular chemistry.[2] It is now of great interest to investigate the usage of non-covalent interactions in networking of the individual spin structures of metal complexes, which can be effectively transferred from a single-crystalline bulk state onto substrate surfaces. However, the controlled association and micro-spectroscopic addressing of paramagnetic coordination compounds on solid support remains challenging. It has to be mentioned that the interaction with a surface can exert a significant effect on the molecular geometry, electronic structure and the molecular environment, thus resulting in loss of the pristine magnetic characteristics.[3]

Herein, we describe the observation and determination of exchange-biased quantum tunneling of magnetization (QTM) in a transition metal coordination cluster showing single-molecule magnet[4] (SMM) behavior – the characteristics which are relevant for the implementation of molecular spin qubits[5] in quantum computing. Our efforts have been focused on the cubane-type Ni$^{\text{II}}$ complex with the formula [Ni(μ_3-Cl)Cl(HL·S)]$_4$ (Figure 1) which is made of charge-neutral fragments, the {Ni$_4$Cl$_8$} core and four thio-augmented,[6] pyridyl-alcohol HL·S ligands [4-(pyridin-2-ylmethyl)-2*H*-thiopyran-4-ol, C$_{11}$H$_{15}$NOS]. The synthesis, structure, and magneto-chemistry using standard SQUID technique (0.1–5.0 T and 2.0–290 K) for this compound were reported[7] previously.

The present study attempts to provide further insights into the magnetic properties of [Ni(μ_3-Cl)Cl(HL·S)]$_4$ at the intermolecular interfaces from the ‘micro-SQUID-on-a-crystal’[8] perspective. Embedding of high dense, stable arrays of metal complexes into surfaces is one of the important goals for achieving practical electrical contacts between single-molecule magnetic units.[9] It is noteworthy that molecular adsorption of [Ni(μ_3-Cl)Cl(HL·S)]$_4$ from solution on the Au(111) surface was recently assessed[10] by X-ray photoelectron spectroscopy, scanning tunneling microscopy, and low-energy electron diffraction. The results indicated that the organic HL·S ligands play a role of so-called molecular bulk-to-surface transporters of the purely inorganic, central {Ni$_4$Cl$_{4n}$} core (n = 1 or 2) with the stability up to 480 K on gold. Further surface-oriented studies are underway.

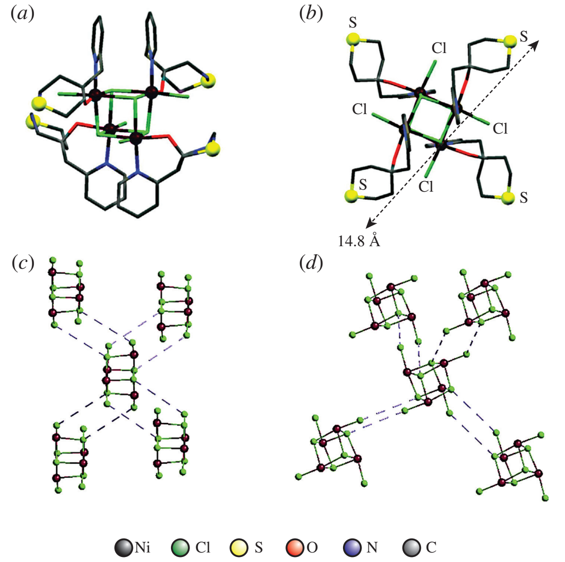


Figure 1 Ball-and-stick representation of (*a*,*b*) the molecular Ni$_4$-SMM structure and (*c*,*d*) the supramolecular {Ni$_4$Cl$_8$} networking with all weak Cl···Cl contacts of *ca.* 6.276 Å in the crystal structure. In (*c*,*d*) the HL·S ligands are omitted for clarity.

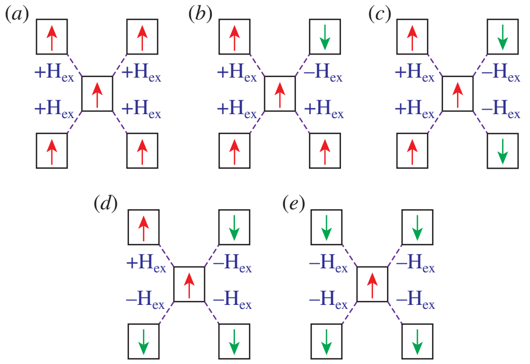


Figure 2 Schematic view of the exchange-coupled network of Ni_4-SMM molecules with different numbers of reversed neighbors.

Figure 1 showcases the molecular and crystal structure of the nickel(II) coordination cluster being in an environment of four exchange-coupled neighbors *via* Cl···Cl intermolecular interactions which lead to an antiferromagnetic super-exchange interaction between pairs of the neutral $\{Ni_4Cl_8\}$ units. Note that each Ni_4-SMM can be treated as a giant spin of $S = 4$ with easy-axis anisotropy. In the applied field the spins of the four neighboring molecules are either aligned with the central one or reversed, thus resulting in five different situations schematized in Figure 2. The influence of the exchange coupled neighboring molecule is taken into account by an exchange-bias field H_{ex} that shifts the QTM step (resonance tunneling) to a new field position. In the case of two reversed neighbors, the net bias is zero, leading to a zero field step [Figure 2(*c*)].

The first derivative (dM/dH) of the magnetization was plotted against magnetic field at different sweep rates [Figure 3(*a*)] in order to obtain an understanding of the fine pattern in the hysteresis loops close to zero field. With the increase of sweep rates the step patterns do not change markedly, which is typical for molecular exchange-biased systems. On scanning to positive fields two steps with almost equal step separation, that is symmetric about zero field, were identified.

Next, the hysteresis loop collected at 0.03 K and at a sweep rate of 0.07 T s^{-1} as a representative was studied in detail. The step-like fine pattern of the title compound depicted in Figure 3(*b*),(*c*) can be explained by exchange coupling between the nearest $\{Ni_4Cl_8\}$ neighbors in the crystal structure of $[Ni(\mu_3\text{-}Cl)Cl(HL{\cdot}S)]_4$. The loop on scanning from negative to positive fields indicates the first QTM step before zero field, confirming weak antiferromagnetic interactions between the cubane-type units. Overall, this Ni_4-SMM clearly shows an antiferromagnetic exchange bias of *ca.* –0.1, –0.05, 0.05 and 0.1 T.

The weak super-exchange interaction between pairs of the $\{Ni_4Cl_8\}$ units was addressed from the bias field detected from QTM steps of the loops based on the following equation:[11]

$$H_{bias} = \sum_{i=1}^{4} H_{bias}^{(i)} = \sum_{i=1}^{4} \frac{2J}{g\mu_B\mu_0} M^{(i)},$$

where M is the quantum number of the neighboring molecule and J is the associated exchange coupling. At low temperatures, M has two possible values, $M = \pm S = \pm 4$. A fit to the acquired data points out that the compound has an intermolecular antiferromagnetic coupling J_{inter} of –0.004 K. This is in line with the previous observations made for exchange-biased, tetranuclear transition metal SMM complexes (Ni_4,[12] Fe_4,[13] and Mn_4[11,14]), suggesting that the intermolecular couplings must be much smaller than the intramolecular ones.

In summary, we have detected intermolecular exchange coupling between neighboring cubane-type $[Ni(\mu_3\text{-}Cl)Cl(HL{\cdot}S)]_4$ coordination clusters *via* exchange-biased QTM in the ground-state, which is clearly manifested by steps in the hysteresis loop measurements. The results described herein might prompt spectroscopy studies with regard to the spin structure and spin transport behavior of this SMM material in the form of supramolecular network on substrate surfaces in the presence of an applied magnetic field.

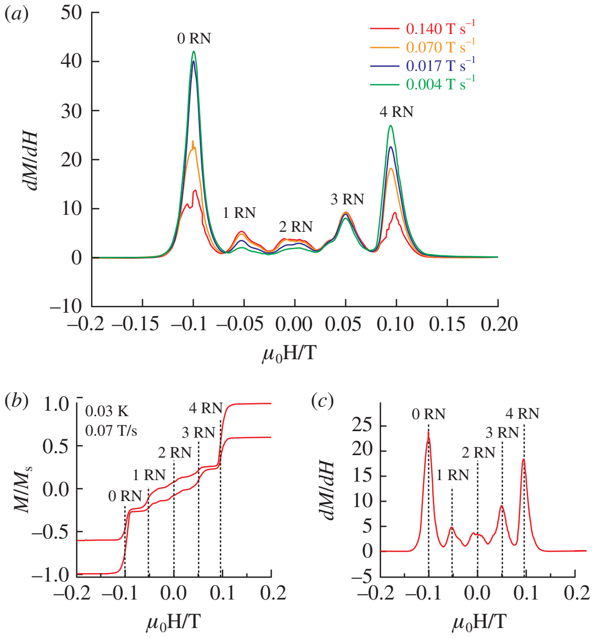


Figure 3 (*a*) Plots of the first derivative (*dM*/*dH*) of the magnetization *versus* magnetic field close to zero field at different sweep rates. The exchange bias of five situations of 0 to 4 reversed neighbors (RN) are indicated. (*b*) Hysteresis loop measured at 30 mK and at a sweep rate of 0.07 T s^{-1}. (*c*) Plot of the first derivative (*dM*/*dH*) of the magnetization against magnetic field close to zero field. The exchange bias of five situations of 0 to 4 reversed neighbors (RN) is indicated.

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