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The magnetic behavior of the nickel cubane complex [Ni₄(OMe)₄-(sal)₄(MeOH)₄] (Hsal = salicylaldehyde) was studied by using a Hartshorn bridge equipped with a ³He/⁴He dilution refrigerator. This complex has long been known to have a well-isolated high-spin ground state with *S* = 4 and it was suggested to have an easy-axis type anisotropy. AC magnetic susceptibility data clearly show a slow magnetization reversal below 0.3 K, characteristic of single-molecule magnets. The Arrhenius plot of the relaxation rate provides the activation energy of about 5 K.

Keywords single-molecule magnet; nickel cubane complex; ac magnetic susceptibility; activation barrier; easy-axis anisotropy

INTRODUCTION

Single-molecule magnets (SMM's) are of growing interest and have been extensively studied in the last decade[1]. Known SMM's are exclusively polynuclear metal complex compounds including $[\text{Mn}_{12}\text{O}_{12}(\text{RCOO})_{16}(\text{H}_2\text{O})_4]$ ($S = 10$)[2], $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$ ($S = 10$)[3], $[\text{Mn}_4\text{O}_3\text{Cl}(\text{OAc})_3(\text{dbm})_3]$ ($S = 9/2$)[4], $[\text{Mn}_4(\text{OAc})_2(\text{pdmH})_6]^{2+}$ ($S = 9$)[5], $[\text{V}_4\text{O}_2(\text{RCOO})_7(\text{bpy})_2]^+$ ($S = 3$)[6], $[\text{Fe}_4(\text{OMe})_6(\text{dpm})_6]$ ($S = 5$)[7], $[\text{Fe}_{19}(\text{metheidi})_{10}(\text{OH})_{14}\text{O}_6(\text{H}_2\text{O})_{12}]^+$ ($S = 33/2$)[8], $[\text{Co}_9[\text{W}(\text{CN})_8](\text{MeOH})_{24}]$ ($S = 21/2$)[9], and $[\text{Fe}_4(\text{sae})_4(\text{MeOH})_4]$ ($S = 8$)[10]. All of these complexes satisfy two essential requirements: a large ground state spin and a large easy-axis type magnetic anisotropy. This results in an appreciable energy barrier for the reversal of the direction of molecular magnetization.

The magnetization reversal barriers are conveniently detected by ac magnetic susceptibility measurements[11] or magnetic hysteresis loop measurements[12]. The former provides directly the barrier height *via* the Arrhenius plot of frequency-temperature dependent susceptibility data, whereas the latter is useful in determination of the blocking temperature (T_B) below which the magnetization reversal by thermal excitation is prohibited and a molecular spin functions as a permanent magnet. This crossover from paramagnets to permanent magnets is not an equilibrium phase transition but a kinetic freezing process leading to a non-ergodic (glassy) state.

A remarkable feature of SMM's is magnetization tunneling. Although their magnetic properties are very similar to those of conventional superparamagnets, which consist of fine particles of single-domain ferro or ferrimagnets, SMM's are different in that they are individual molecules with uniform size and shape. Due to this monodispersivity, it is possible to observe quantum-mechanical tunneling of magnetization. SMM's are thus ideal model systems for the detailed study of dissipative tunneling phenomena[13].

The title compound, $[\text{Ni}_4(\text{OMe})_4(\text{sal})_4(\text{MeOH})_4]$, has long been known to have a large-spin ground state with $S = 4$, arising from a ferromagnetic intracuster interaction $J/k_B = 5.8 \text{ K}$ [14-15]. In 1983 Sorai *et al.* reported the magnetic heat capacity of this compound [16]. Their analysis bore out a spin energy-level scheme featuring a molecular spin $S = 4$ with easy-axis type anisotropy and suggested an energy barrier for magnetization reversal of about $4 k_B \text{ K}$. This result prompted us to examine the dynamics of magnetization of this Ni_4 cubane complex at low temperatures.

EXPERIMENTAL

A powder sample of $[\text{Ni}_4(\text{OMe})_4(\text{sal})_4(\text{MeOH})_4]$ was prepared by refluxing the mononuclear complex $[\text{Ni}(\text{sal})_2(\text{MeOH})_2]$ with MeONa in methanol as described in the literature [15]. The tetranuclear species was isolated by ethyl ether extraction of the solid residue obtained after solvent removal. This was further purified by recrystallization in methanol.

Complex magnetic susceptibility measurements were carried out by the Hartshorn bridge method using a variable mutual inductor (H. Tinsley & Co., Type 4229) and a homemade phase potentiometer. A Lock-in amplifier (Princeton Applied Research, Model 124A) served as an alternating current source and a phase-sensitive zero-point detector of the bridge. A polycrystalline sample was mounted with a small amount of Apiezon N grease on an oxygen-free copper rod screwed into a mixing chamber of a $^3\text{He}/^4\text{He}$ dilution refrigerator. Throughout the experiments, temperature measurements were performed using a germanium resistor thermometer calibrated to the Greywall scale and an ac resistance bridge (RV Elektronikka, AVS-46). The temperature region of the study was 100 mK - 2 K and the ac frequency was varied between 200 Hz - 3 kHz.

RESULTS AND DISCUSSIONS

The complex magnetic susceptibilities of $[\text{Ni}_4(\text{OMe})_4(\text{sal})_4(\text{MeOH})_4]$ are shown in FIGURE 1. The real part (χ'_m) measured in 3.02 kHz ac field obeys the Curie-Weiss law above 1 K, where the paramagnetic Curie temperature is about -0.5 K suggesting the presence of small antiferromagnetic intercluster interactions. On cooling, the value of χ'_m shows a deviation from the Curie-Weiss behavior below 0.5 K. The χ'_m value reaches a maximum at 0.26 K below which a remarkable drop is seen. The imaginary part (χ''_m) shows a remarkable enhancement below 0.3 K, characteristic of freezing of magnetization reversal.

The frequency dependence of the complex susceptibility $\chi_m(\omega)$ suggests a relaxation process *via* a thermal activation mechanism. The out-of-phase ac susceptibility data (χ''_m) were analyzed using the Arrhenius law; an activation energy of $5.3 k_B$ K was calculated. This value is in good agreement with the energy barrier for magnetization reversal of *ca.* $4 k_B$ K estimated from magnetic heat capacity data[16].

Based on a classical vector picture, the energy barrier for magnetization reversal appears to have two possible origins: a collinear easy-axis alignment or an orthogonal hard-axis alignment of

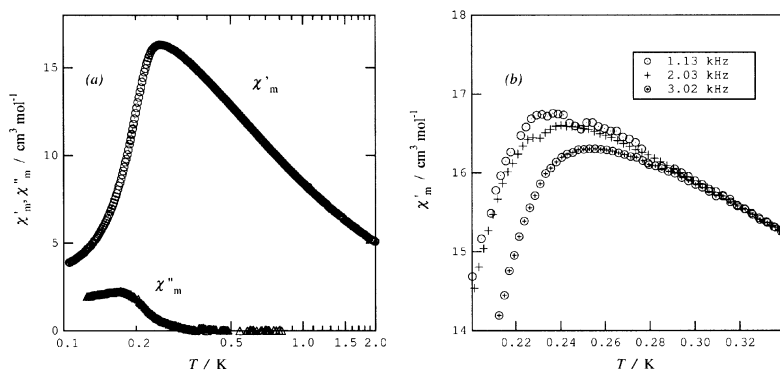


FIGURE 1 Complex susceptibilities of $[\text{Ni}_4(\text{OMe})_4(\text{sal})_4(\text{MeOH})_4]$. (a), Real and imaginary part measured at 3.02 kHz; (b), frequency dependence of the real part near freezing temperatures.

single-ion spins (see FIGURE 2). The coordination geometry of this nickel cubane complex suggests the latter option is the case. This can be explained as follows. Consider an anisotropic spin pair with strong ferromagnetic coupling as a simplest model system:

$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 + D\hat{S}_{1x}^2 + D\hat{S}_{2y}^2, \quad (1)$$

where we assume a strong coupling limit, $J \gg D > 0$. This spin Hamiltonian is easily rewritten by introducing a resultant spin operator, $\hat{S} = \hat{S}_1 + \hat{S}_2$, to provide

$$\hat{H} = J[\hat{S}_1^2 + \hat{S}_2^2 - \hat{S}^2] - (D/2)[\hat{S}_z^2 - 2\hat{S}_{1z}\hat{S}_{2z} - (\hat{S}_1^2 + \hat{S}_2^2)] + \hat{H}_1, \quad (2)$$

$$\hat{H}_1 = (D/2)[(\hat{S}_{1x}^2 - \hat{S}_{1y}^2) - (\hat{S}_{2x}^2 - \hat{S}_{2y}^2)]. \quad (3)$$

Confining to a ground spin manifold $|S, M_s\rangle$, the first term in the

Hamiltonian (2) is obviously a constant. The third term \hat{H}_1 contributes off-diagonal elements, but is not significant in the large- J limit. Although the product $\hat{S}_{1z}\hat{S}_{2z}$ in the second term causes mixing with higher S manifolds, a usual projection procedure[17] is allowed in the large- J limit as $\hat{S}_i = p_i\hat{S}$, where

$$p_i = 1/2 + [S_i(S_i + 1) - S_{3-i}(S_{3-i} + 1)]/2S(S + 1). \text{ Substituting } \hat{S}_{1z}\hat{S}_{2z}$$

by $p_1p_2\hat{S}_z^2 = (1/4)\hat{S}_z^2$, the second term turns out to represent molecular

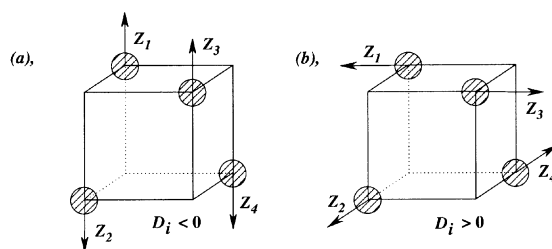


FIGURE 2 S_4 -symmetry spin cluster consisting of ferromagnetically-coupled 4 single-ion spins with (a), collinear easy-axis alignment; (b), orthogonal hard-axis alignment. Both of the cases provide an easy-axis type anisotropy of the resultant spin.

easy-axis character $-(D/4)\hat{S}_z^2$ derived from positive single-ion D . It may also become useful as another guide to design novel SMM's.

In conclusion, we examined ac magnetic susceptibilities of the nickel cubane complex, $[\text{Ni}_4(\text{OMe})_4(\text{sal})_4(\text{MeOH})_4]$, and found slow magnetization relaxation attributed to slow dynamics of molecular spin reversal. The effective energy barrier of magnetization reversal was estimated to be $5.3 k_B \text{ K}$.

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