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[Ni(en)(H₂O)₄][SO₄] · 2H₂O — an $S = 1$ Molecular Magnet with Easy-Plane Anisotropy

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Structural analysis of [Ni(en)(H₂O)₄][SO₄] · 2H₂O was performed and it suggests that the crystal field should play a dominant role in the magnetic properties of the system. This conjecture coincides well with the specific heat and susceptibility behaviour. The analysis confirmed that the compound can be treated as a spin 1 single molecule magnet with nonmagnetic ground state introduced by easy-plane single-ion anisotropy $D/k_B \approx 11$ K and neglecting in-plane anisotropy $E/D < 0.1$.

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1. Introduction

Two-dimensional (2D) frustrated spin systems have attracted much attention since they can exhibit unconventional magnetism [1]. Recently, we studied magnetic properties of a molecular magnet Cu(en)(H₂O)₂SO₄ (en = ethylenediamine) which is a representative of the $S = 1/2$ spatially anisotropic triangular lattice [2]. The specificity of this material is based on the fact that the magnetic lattice is formed of unconventional exchange bridges supported by hydrogen bonds (HBs). The present work is devoted to the experimental study of magnetostructural correlations of nickel(II) analogue of Cu(en)(H₂O)₂SO₄, a potential representative of an $S = 1$ spatially anisotropic triangular lattice characterized by the competition between quantum fluctuations, geometrical frustration and single-ion anisotropy.

2. Experimental details

[Ni(en)(H₂O)₄][SO₄] · 2H₂O (NEHS) has been synthesized in the form of blue prisms from an aqueous solution of nickel sulphate and en in stoichiometric

amounts. X-ray single crystal studies revealed that the structure of the compound is already known and was published in the work [3]. NEHS crystallizes in the monoclinic system with the unit cell parameters $9.523 \times 12.185 \times 11.217 \text{ \AA}^3$. The crystal structure of the compound is built of $[\text{Ni}(\text{en})(\text{H}_2\text{O})_4]^{2+}$ cations, $[\text{SO}_4]^{2-}$ anions and two water molecules comprising basic structural units. The units are mutually connected by a large number of HBs forming a three-dimensional crystal structure (Fig. 1). Considering magnetic orbitals of Ni(II) ion in octahedral surroundings, the magnetic system can be viewed as a 3D array of coupled $S = 1$ triangular layers.

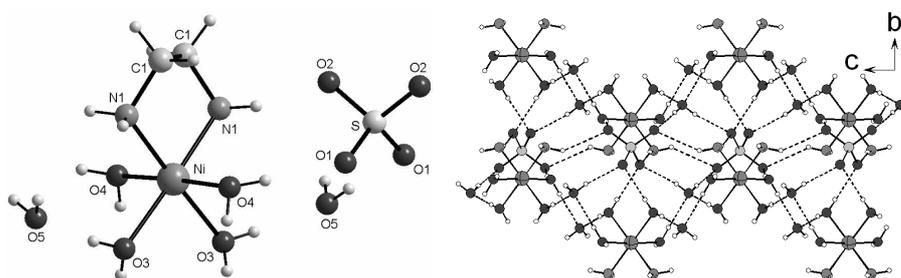


Fig. 1. Structural unit of NEHS (left). Projection of the crystal structure into the bc plane. The hydrogen bonds are presented by dashed lines (right).

Specific heat measurements of 7 mg single crystal have been performed on a commercial PPMS system. Since the exposure of the sample to a high vacuum leads to a massive release of water molecules and subsequent deterioration of the structure, the crystals were coated by a layer of Apiezon N. Magnetic susceptibility studies of a powder sample with a mass of 130 mg have been performed in a commercial SQUID magnetometer. The addenda to specific heat and susceptibility has been determined in separate runs.

3. Results and discussion

The specific heat was experimentally studied in zero magnetic field in the temperature range from 1.8 to 30 K. The behaviour of the data is dominated by a round anomaly at 4.4 K and a monotonic increase is observed at higher temperatures (Fig. 2a). Since NEHS represents a magnetic insulator, the total specific heat, C_{tot} , is determined by the phonon contribution, C_{ph} and magnetic subsystem, C_{mag} . For a quantitative analysis of magnetic specific heat, the lattice contribution has been subtracted. The standard procedure based on the finding of a temperature region where the approximation $C_{\text{mag}} \approx a/T^2$ and $C_{\text{ph}} \approx bT^3$ works, provided overestimation of the lattice contribution (Fig. 2a), thus, a higher term has been introduced in the phonon specific heat, $C_{\text{ph}} \approx bT^3 + cT^5$. The fitting procedure performed in the range from 12 to 20 K yielded much more realistic estimation of both, lattice and magnetic specific heat. The corresponding

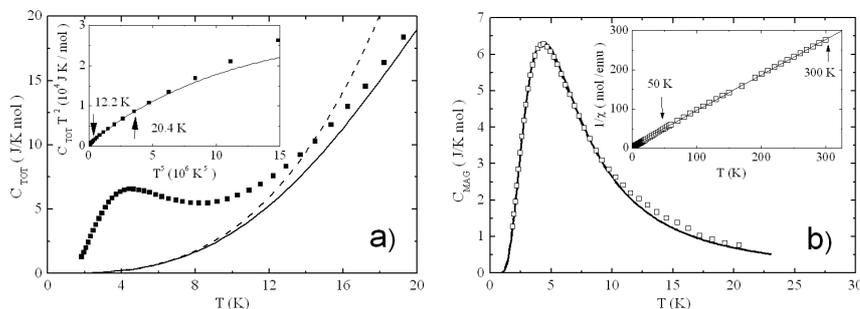


Fig. 2. (a) Temperature dependence of NEHS specific heat in zero magnetic field (squares). The solid line represents a lattice contribution, the dashed line represents the contribution of a standard Debye T^3 law. Inset: CT^2 vs. T^5 (squares), solid line represents the fit $y = a + bx + cx^{1.4}$ with $x = T^5$, $y = CT^2$. The arrows indicate the fitting interval. (b) Temperature dependence of magnetic specific heat of NEHS (squares). Nearly indistinguishable solid and dashed lines represent the $S = 1$ paramagnet with $E/D = 0$, $D/k_B = 11.6$ K and $E/D = 0.1$, $D/k_B = 11.6$ K, respectively. Inset: Temperature dependence of inverse susceptibility of NEHS (squares). The solid line represents Curie–Weiss law with $g = 2.1$ and Curie temperature $\Theta_C \approx -7$ K. The arrows indicate the fitting interval.

coefficients have been obtained, $a = 312$ J K/mol, $b = 0.00345$ J/(K⁴mol) and $c = -2.7 \times 10^{-6}$ J/(K⁶ mol). Assuming 9 vibrating groups in the NEHS molecule, the Debye temperature $\Theta_D \approx 170 \pm 5$ K has been evaluated from the b coefficient. The rather low value of Θ_D reflects a softness of the structure resulting from the low-energetic hydrogen bonds providing intermolecular contacts.

The analysis of the crystal structure suggests that the hydrogen bonds also support the formation of unconventional exchange paths mediating exchange coupling between $S = 1$ spins within a triangular layer and between the layers. Considering the elongation of local octahedral surroundings of Ni(II) ion, uniaxial single-ion anisotropy can be expected to control magnetic properties of NEHS. Following the approach applied in Ref. [4] for heteroleptic complexes, we estimated the effective elongation of the octahedron $D_{\text{structure}} \approx 14$ pm which corresponds to the single-ion anisotropy parameter $D/k_B \approx 12$ K while in-plane anisotropy parameter, E/k_B , related to the rhombic distortion of the octahedron, has been neglected. The large anisotropy value enables the application of the relation $a = (R/2)(D/k_B)^2$, from which the value of single-ion anisotropy constant $D/k_B = 8.5 \pm 1.5$ K has been estimated. After subtracting the lattice contribution, the magnetic entropy was calculated from the magnetic specific heat data in the region from 1.8 K to 20 K. A standard extrapolation was employed in the interval from 20 K to $T \rightarrow \infty$, while missing specific heat data below 1.8 K have been extrapolated by an exponential decrease as expected for the systems with dominant single-ion anisotropy effects. The good agreement between the experimental

value $S = 9.56 \pm 0.50$ J/(K mol) and the theoretical entropy $R \ln(2S + 1)$ for spin 1 indicates the absence of a phase transition to the ordered state below 1.8 K. Consequently, in the first approximation, the magnetic specific heat data have been analyzed within a simple model of a spin 1 paramagnet with energy levels split by a crystal field described by D and E parameters in the spin Hamiltonian $H = DS_z^2 + E(S_x^2 - S_y^2)$.

The best agreement was found for the easy-plane model with $E/D < 0.1$ and $D/k_B = 11.6 \pm 1.5$ K (Fig. 2b). The obtained parameters correspond well with those obtained from the structural analysis. Magnetic susceptibility has been measured in the temperature range from 1.8 to 300 K in the field 10 mT. No difference has been observed between the data obtained in the field cooling and zero-field cooling regimes. The susceptibility has been corrected for the contribution of core diamagnetism which was estimated using the Pascal constants $\chi = -179.1 \times 10^{-6}$ emu/mol. The data above 50 K are well characterized by a Curie–Weiss law with $g = 2.1$ and Curie temperature $\Theta_C \approx -7$ K corresponding to the combined effect of single-ion anisotropy and exchange coupling. The potential texture effect cannot be excluded (Fig. 2b).

In conclusion, our experimental studies indicate that at temperatures above 2 K $[\text{Ni}(\text{en})(\text{H}_2\text{O})_4][\text{SO}_4]_2 \cdot \text{H}_2\text{O}$ can be classified as a spin 1 single-molecule magnet with nonmagnetic ground state. In the near future, further experiments will be performed to estimate the strength of intermolecular exchange coupling. The interplay of geometrical frustration, single-ion anisotropy and sufficiently large magnetic fields is expected to introduce interesting quantum effects at temperatures comparable with the strength of magnetic correlations.

Acknowledgments

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