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Field-Induced Slow Magnetic Relaxation in Mn_9W_6 Cluster-Based Compound

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Magnetic measurements of a three-dimensional (3D) molecular magnet built of $\text{Mn}_9[\text{W}(\text{CN})_8]_6$ clusters have been carried out to study its static and dynamic properties. Measurements of ac susceptibility in the presence of static magnetic field revealed slow magnetic relaxations. It was found that for the 120 Hz wave frequency the optimal static field which maximizes the imaginary component of the ac susceptibility is about 500 Oe.

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1. Introduction

Polynuclear clusters are studied widely by both chemists and physicists for their magnetic, optical and electronic properties [1–4]. High-nuclearity clusters based on magnetically coupled paramagnetic ions can often reveal a high-spin ground state. An intensively studied group of polynuclear clusters are those showing slow magnetic relaxation, such as the famous Mn_{12} [5]. The reason for this great interest is related to their potential application in spin-based devices [6]. In most cases compounds which reveal slow magnetic relaxations are based on magnetic ions with significant single ion anisotropy such as Co^{II} , Fe^{II} , Mn^{III} or rare-earth metals. In the present paper we study magnetic properties of $\text{Mn}_9^{\text{II}}[\text{W}^{\text{V}}(\text{CN})_8]_6(\text{ald-4})_4(\text{MeOH})_{18} \cdot 4\text{MeOH}$ (**1**), a 3D cluster based material, whose magnetic properties originate from the Mn^{II} and W^{V} ions. Both of these metal ions present isotropic magnetic properties. However we will show that even for compounds based on isotropic metals slow magnetic relaxations are possible due to structure anisotropy.

2. Experimental

Synthesis. The compound was synthesized via the slow evaporation of the methanol mixture of $\text{Mn}^{\text{II}}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}_3[\text{W}^{\text{V}}(\text{CN})_8] \cdot 1.5\text{H}_2\text{O}$ and aldrithiol-4.

Remarks. The crystals are unstable and exchange solvents to water upon exposure to air. The composition was determined by the crystal structure solution and refinement. The mass of the magnetically active sample was deduced from the recalculation of the molar mass of crystals basing on the composition of the hydrated phase.

Magnetic measurements. All the magnetic data were measured using the Quantum Design MPMS XL magnetometer. The measurements of both components of the

ac susceptibility χ_{ac} were carried out as a function of temperature for various frequencies and as a function of dc field H_{dc} . Dc susceptibility data were obtained field cooled conditions with applied static field of 500 Oe, whereas the isothermal magnetization was detected at 2.0 K in the field range of 0–70 kOe. All measurements were performed on polycrystalline samples which were immersed in a few ml of alcohol solution and closed in a glass tube.

3. Results

The crystal structure is composed of coordination chains of pentadecanuclear cyano-bridged Mn_9W_6 clusters bridged linearly by double sets of 4-aldrithiol spacers along the c direction. The chains are further decorated by other terminal 4-aldrithiol molecules and MeOH molecules. The internal structure of the Mn_9W_6 clusters is topologically identical with those reported recently for this family of compounds [7–9].

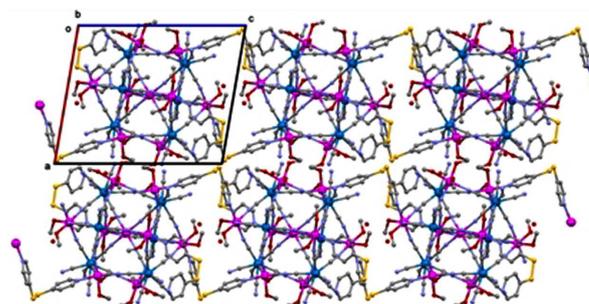


Fig. 1. The view of the crystal structure of **1** along the direction b (magenta — Mn ions, blue — W ions).

One-dimensional (1D) coordination topology in **1** is accompanied by a dense closely packed and nearly isotropic 2D–3D supramolecular cluster based architecture (Fig. 1). The intercluster distances are the closest ever observed for this family of compounds, with the closest hydrogen bonded $\text{W} \cdots \text{Mn}$ contacts of *ca.* 6.69, 6.76, and

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7.32 Å within the *ab* crystallographic layer. The effective interlayer distances are of *ca.* 8.0 Å due to the interlayer slide in the direction orthogonal to the *ab* layer (*c**).

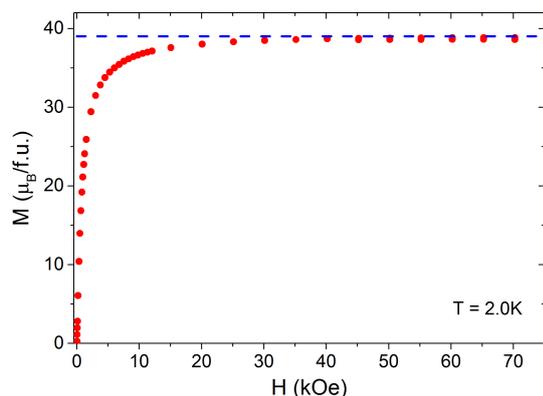


Fig. 2. Isothermal magnetization of **1** at 2.0 K. Red circles represent the measured values and the dashed lines is the 39 μ_B /f.u. .

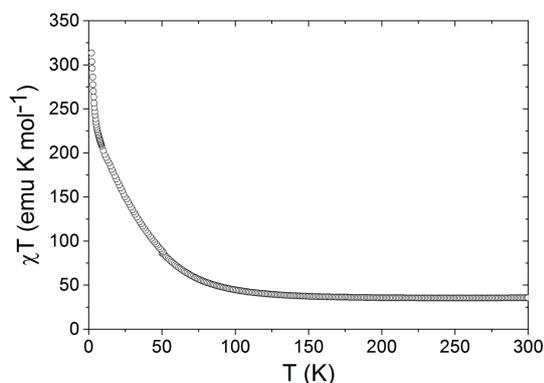


Fig. 3. Temperature dependence of χT measured in the dc field of 500 Oe.

The isothermal magnetization measurement at $T = 2.0$ K (see Fig. 2) reveals saturation of magnetization amounting to 38.9 μ_B /f.u. above about 25 kOe. This value agrees very well with that of 39 μ_B /f.u. expected for antiparallel alignment of magnetic moments of the W^V ($g_W = 2.0$, $S_W = 1/2$) and Mn^{II} ($g_{Mn} = 2.0$, $S_{Mn} = 5/2$) ions inside the cluster. Figure 3 shows temperature dependence of χT . The χT values decrease as the temperature increases. The value of χT at 300 K is 35.6 emu K mol^{-1} , which is lower than 41.7 emu K mol^{-1} expected for uncoupled nine Mn^{II} and six W^V . This discrepancy may be due to antiferromagnetic intramolecular interactions. Similar behaviour was reported in [7].

To study magnetic properties of **1** in more detail, a series of ac susceptibility measurements was performed. The temperature dependences of ac susceptibility for four different frequencies are displayed in Fig. 4a. As can be observed, there are no signatures of any phase transition to long-range magnetic order down to 2.0 K. There is also no evidence of frequency dependence of χ_{ac} . However, the dc field dependence of the imaginary part of ac

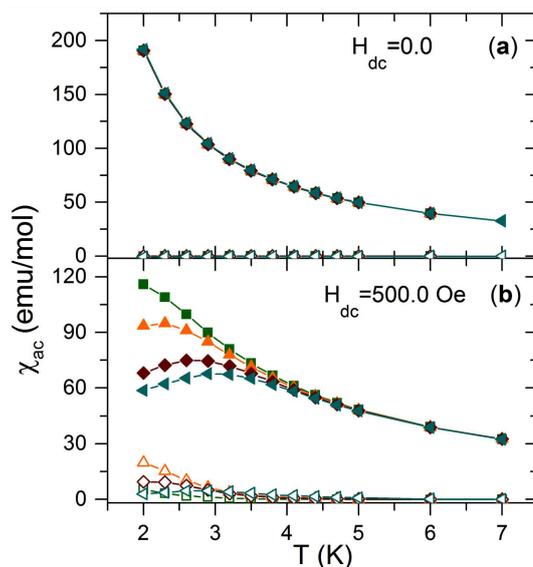


Fig. 4. Ac susceptibility as a function of temperature for frequencies: 0.1 Hz (\blacksquare), 1.0 Hz (\blacktriangle), 10.0 Hz (\blacklozenge) and 997.3 Hz (\blacktriangleleft). Full symbols represent the in-phase component and open symbols show the out-of-phase part for $H_{dc} = 0$ (a) and $H_{dc} = 500$ Oe (b). Points in the top graph lie on top of each other. Solid lines are guides for the eyes.

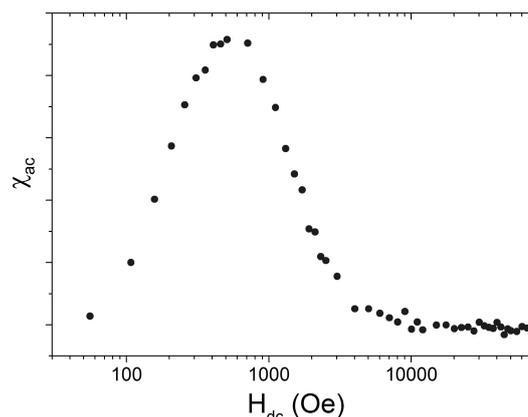


Fig. 5. Dc field dependence of χ''_{ac} measured in temperature of 2.0 K for frequency 120 Hz.

susceptibility (Fig. 5) reveals a broad maximum at about 500 Oe.

Repeated measurements of χ_{ac} as a function of temperature in the presence of dc field of 500 Oe (Fig. 4b) reveal a field induced frequency dependence. Both Mn^{II} and W^V ions are magnetically isotropic, so we can expect that this is also the case with the whole Mn_9W_6 cluster, hence the most likely explanation of this behavior is supramolecular anisotropy affected by intercluster coupling originating from the 4-aldriithiol bridges and the through-space dipole-dipole interaction.

4. Conclusions

The object of the study was the 3D cluster based compound. The magnetic data indicate that the intercluster

interactions between the Mn^{II} and W^V ions are antiferromagnetic and there is no evidence of long-range magnetic order down to 2.0 K.

The measurements of ac susceptibility as a function of external dc field allowed to determine the value of field $H_{dc} = 500$ Oe which optimizes the χ''_{ac} signal. The temperature dependence of the in-field ac susceptibility shows the frequency dependent response indicating field induced slow relaxations. At this stage of preliminary studies the most probable explanation of this result is the anisotropy related to supramolecular structure of the studied compound. However, further experimental studies concerning slow magnetic relaxations are planned to obtain a deeper understanding of this phenomenon.

Acknowledgments

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