

# Theoretical investigations of tetrameric magnetic molecules for sub-kelvin cooling

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Magnetic molecules are a class of compounds that is also investigated in view of their magnetocaloric properties. The isothermal entropy change and the adiabatic temperature change are key figures of merit for magnetocaloric performance. Here, we investigate spin systems of realistic molecular structures comprising four spins. In view of possible large spin quantum numbers as for gadolinium we model these spin systems by a combination of Heisenberg and dipolar spin-spin interactions. It turns out that a tetrahedral structure with ferromagnetic exchange interactions yields the best figures of merit.

## I. INTRODUCTION

One could summarize the efforts in the field of molecule-based magnetocalorics as looking for “recipes for enhanced molecular cooling” [1]. Among the more general recipes is the suggestion to employ frustrated spin systems [2], i.e., systems with competing exchange interactions as for instance given in cuboctahedra or other geometrically frustrated arrangements of spins [3–7]. Here, the idea is to generate an enhanced low-lying density of states that can be manipulated by moderate magnetic fields. If the system is close to a quantum critical point this effect is particularly large [7–10]. On the other hand, spin systems with a large energy gap between the ground state and excited states would not be as well suited.

Such an energy gap occurs for instance in spin systems termed single-molecule magnets that are characterized by a strong easy-axis anisotropy that separates a two-fold degenerate ground state from higher lying levels. However, such spin systems show a rotational magnetocaloric effect that occurs when the magnitude of the magnetic field is kept constant and the sample (or the field) are rotated [11–14]. Although very appealing, technical difficulties such as heat from friction prevent a use at low temperatures so far.

Another trend in the field is to employ lanthanides, in particular gadolinium, because of the large spin and corresponding large number of levels per spin that directly translate into available entropy [15–19]. Larger spins and in particular net spins per molecules might, however, lead to long range magnetic order that precludes the desired low-temperature (sub-kelvin) cooling [20]. Very low temperatures are thus achieved when separating the molecules or spins sufficiently well [21, 22].

In this article, we are going to investigate spin systems composed of four spins with realistic geometries as obtained in chemical synthesis. This investigation is along the ideas of Refs. [23–25] where square-pyramidal structures have been studied employing the Heisenberg model. In our current study, we add intramolecular dipolar interaction which can be sizable for larger spins [26]. It also plays an important role below about one kelvin.

Our investigations suggest that tetrahedral arrangements of spins with ferromagnetic exchange interactions yield the strongest magnetocaloric effect. Furthermore, among the investigated structures it is the only arrangement that is able to achieve very low temperatures. We will substantiate our findings with a comparison of four typical structures, however, limit our self to a few central graphs. The reader is encouraged to have a look at a recent Ph.D. thesis offering detailed explorations of the possible huge parameter space [27].

The paper is organized as follows. In Section II we introduce the model and major observables before we present our results in Sec. III. The article closes with a discussion in Section IV.

## II. MODEL

In the present study we employ a Hamiltonian that consists of Heisenberg exchange interactions as well as dipolar interactions,

$$\begin{aligned} \tilde{H} = & \sum_{i<j} J_{ij} \tilde{s}_i \cdot \tilde{s}_j + g\mu_B B_z \sum_i \tilde{s}_i^z \\ & + \frac{\mu_0\mu_B^2}{4\pi} \sum_{i<j} \frac{g^2}{r_{ij}^3} \left( \tilde{s}_i \cdot \tilde{s}_j - 3 \cdot \tilde{s}_i \cdot \vec{e}_{ij} \otimes \vec{e}_{ij} \cdot \tilde{s}_j \right). \end{aligned} \quad (1)$$

Here,  $\tilde{s}_i$  denotes the spin vector operator at site  $i$ , and a tilde is used to denote operators in general. The Zeeman term is assumed along the global  $z$ -direction, thus the molecules have to be rotated to investigate the influence of the relative orientation which, however, is expected to be small since the anisotropic effect of the dipolar interaction is small. Therefore, we will show only one chosen direction for each example. In addition, we fix  $g = 2$  in the following. Single-ion anisotropy is not considered in this study although of course potentially also important, compare e.g. [28, 29].

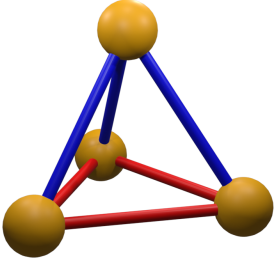
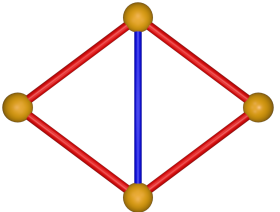
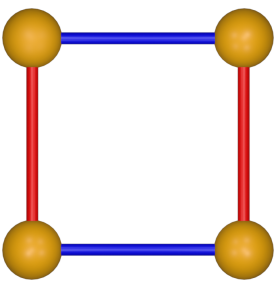

The spin systems are treated by exact diagonalization. Thermal equilibrium observables are calculated in the canonical ensemble. We concentrate on realistic exchange interactions and a realistic field change from  $B = 7$  T to  $B = 0$  when evaluating the isothermal entropy change.

In the following we consider four different typical spin systems as listed in table I, a tetrahedron, a butterfly

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Table I. Investigated structures and considered exchange interactions.  $J_1$  is shown in red,  $J_2$  in blue.


$J_1 = J_{\text{base}} = \{J_{12}, J_{23}, J_{13}\}, J_2 = J_{\text{top}} = \{J_{14}, J_{24}, J_{34}\}$

$J_1 = J_{\text{wings}} = \{J_{12}, J_{23}, J_{34}, J_{14}\}, J_2 = J_{\text{body}} = \{J_{13}\}$

$J_1 = J_{\text{outer}} = \{J_{12}, J_{34}\}, J_2 = J_{\text{inner}} = \{J_{23}\}$

$J_1 = J_{\text{ver}} = \{J_{12}, J_{34}\}, J_2 = J_{\text{hor}} = \{J_{23}, J_{14}\}$

system, a linear chain, and a square. We allow two different exchange interactions in our search for advantageous coupling schemes.

### III. RESULTS

In the following we discuss four typical motives as they appear in molecular compounds. We show isothermal entropy changes in the parameter space of  $J_1$  and  $J_2$  for the spin quantum number  $s = 3/2$  for a field sweep from  $B = 7$  T down to  $B = 0$ . The Heisenberg limit is denoted as  $d = \infty$ , i.e., for zero dipolar interaction. In order to account for dipolar influence we picked some reasonable (but not too large) distances. It is clear that the parameter space of such an investigation is practically limitless since one could vary the spin quantum numbers, introduce more exchange constants, and vary the distances that are important for the dipolar interaction in a much

larger range.

Here we focus on central and typical results, the reader is invited to have a look at the wealth of simulation results presented in the Ph.D. thesis [27].

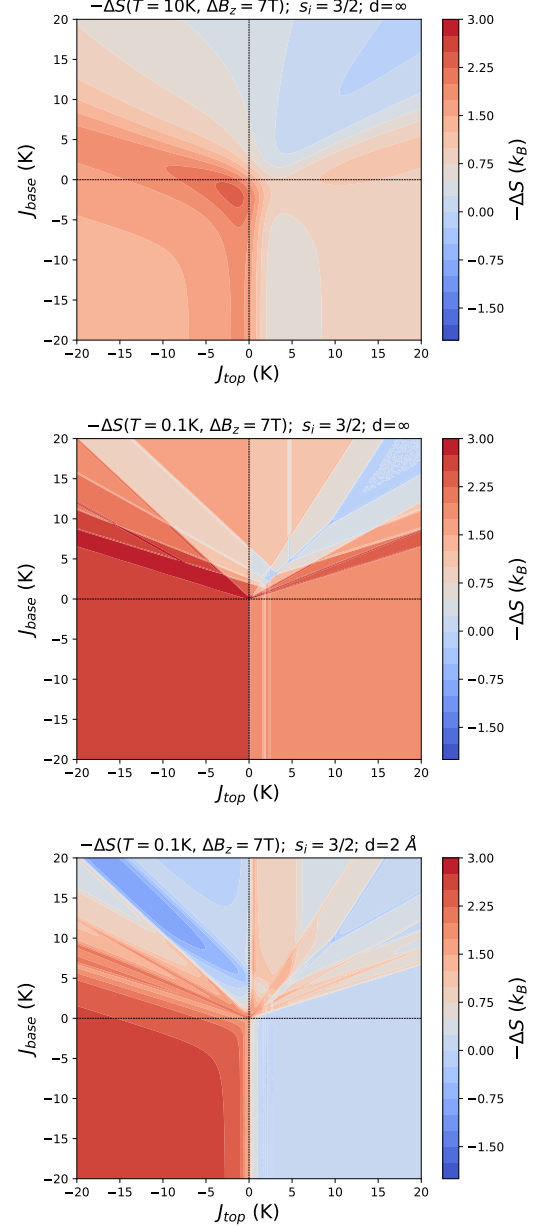


Figure 1. Isothermal entropy change for a tetrahedron with  $s = 3/2$  at  $T = 10$  K (top),  $T = 0.1$  K (middle), and  $T = 0.1$  K (bottom); the latter including dipolar interactions for a distance of  $d = 2$  Å. The magnetic field is perpendicular to the plane of the red triangle in the tetrahedron, see Tab. I. The color maps show the respective entropy changes.

For the discussion of the isothermal entropy change we picked two temperatures,  $T = 10$  K and  $T = 0.1$  K, again more in [27]. The behavior at  $T = 0.1$  K without dipolar interactions is then contrasted with the behavior including dipolar interactions. At  $T = 10$  K the dipolar



interaction has practically no effect.

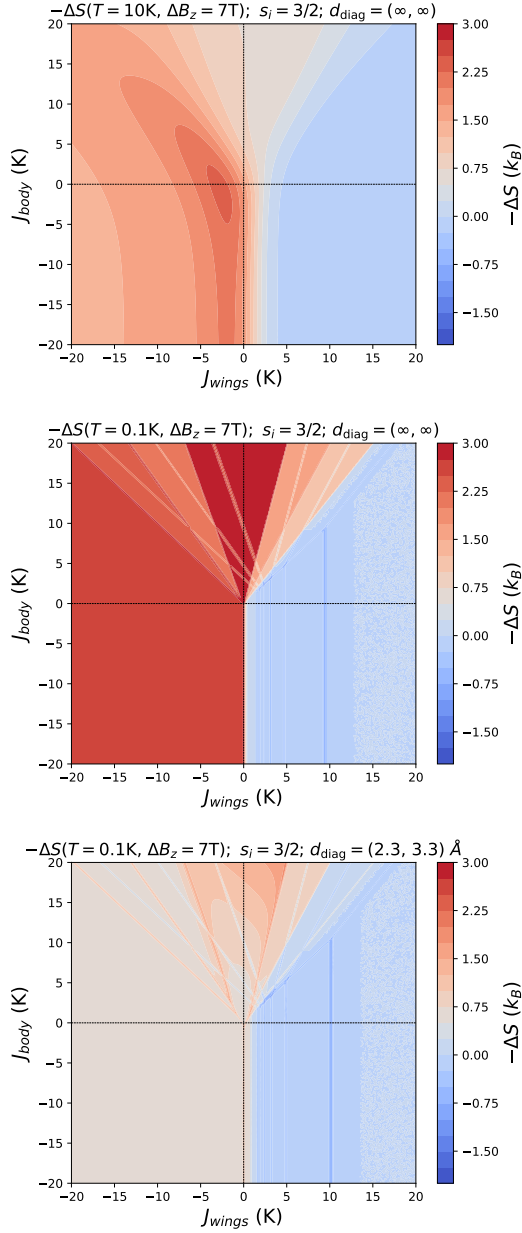


Figure 2. Isothermal entropy change for a butterfly with  $s = 3/2$  at  $T = 10$  K (top),  $T = 0.1$  K (middle), and  $T = 0.1$  K (bottom); the latter including dipolar interactions for distances of  $d_1 = 2.3$  Å (corresponding to  $J_{13}$ ) and  $d_2 = 3.3$  Å (corresponding to  $J_{24}$ ). The magnetic field points along the longer diagonal of the butterfly corresponding to  $J_{24}$ , see Tab. I. The color maps show the respective entropy changes.

At  $T = 0.1$  K the dipolar interaction has got an important effect. Without dipolar interaction the largest isothermal entropy change is typically achieved for non-interacting spins. This is unrealistic since at small enough temperatures the effect of dipolar interactions will not only be visible, it will be unavoidable. In molec-

ular magnetism this typically happens below 1 K. Therefore, when discussing sub-kelvin cooling the dipolar interaction has to be taken into account.

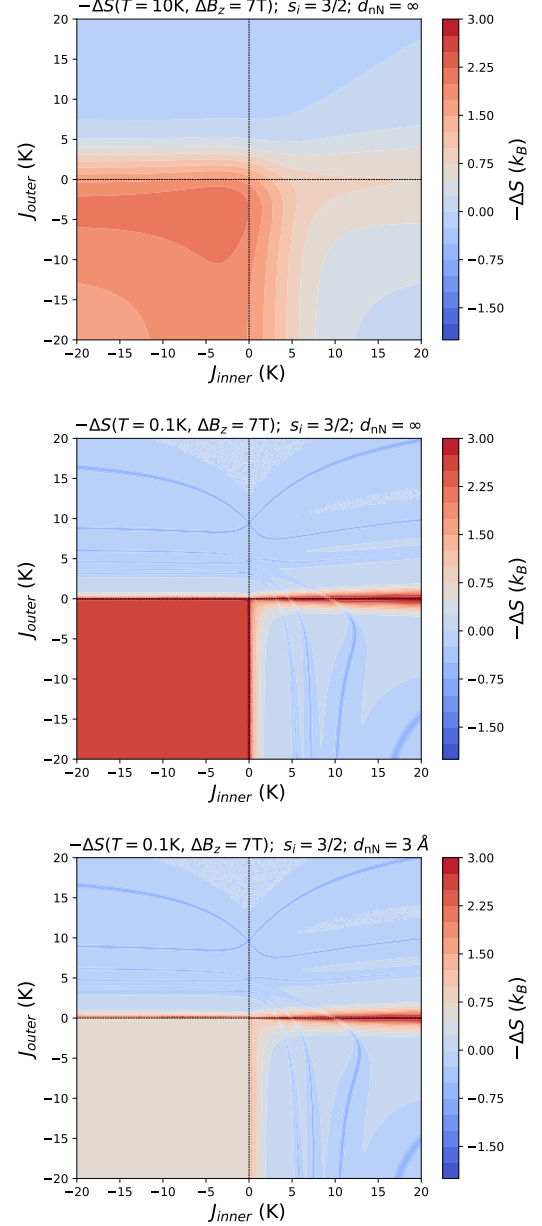


Figure 3. Isothermal entropy change for a chain with  $s = 3/2$  at  $T = 10$  K (top),  $T = 0.1$  K (middle), and  $T = 0.1$  K (bottom); the latter including dipolar interactions for distances of  $d = 3$  Å. The magnetic field points along the axis of the chain. The color maps show the respective entropy changes.

Figure 1 shows the isothermal entropy change for a tetrahedron with spin quantum number  $s = 3/2$ . The upper and middle panel are for  $T = 10$  K and  $T = 0.1$  K, respectively, both without dipolar interactions. The lower panel displays the situation at  $T = 0.1$  K with dipolar interaction. The most reddish parts denote the largest



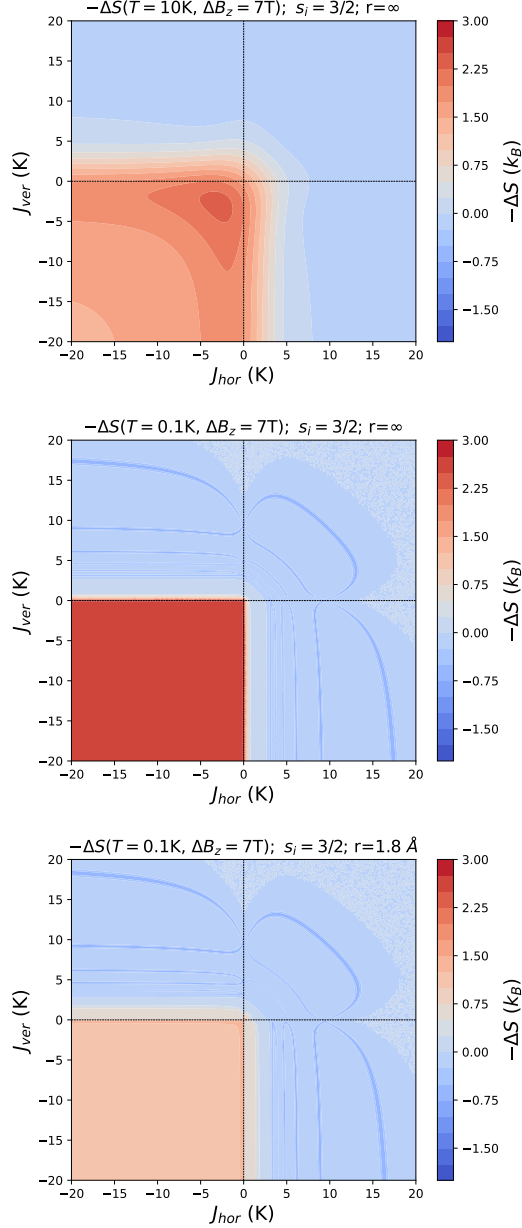


Figure 4. Isothermal entropy change for a square with  $s = 3/2$  at  $T = 10$  K (top),  $T = 0.1$  K (middle), and  $T = 0.1$  K (bottom); the latter including dipolar interactions for distances of  $d = 2.54$  Å between adjacent spins. The magnetic field points along two parallel edges of the square. The color maps show the respective entropy changes.

isothermal entropy changes. For  $T = 10$  K, where the dipolar interaction does not play much of a role, the optimal molecule would possess very small and slightly ferromagnetic couplings. For  $T = 0.1$  K, one notices that the very large isothermal entropy change in the quadrant of both ferromagnetic exchange interactions is not much altered by dipolar interactions. This robust behavior singles out the tetrahedron among the discussed four-spin structures.

The butterfly and the chain, Figs. 2 and 3, lose their good isothermal entropy changes for ferromagnetic couplings at sub-kelvin temperatures when the dipolar interaction is taken into account. This effect is rather drastic as can be seen in the bottom panels of both figures. For  $T = 10$  K, the chain shows good isothermal entropy changes for small ferromagnetic interactions whereas the butterfly performs good for ferromagnetic  $J_{\text{wings}}$  independent of the sign of  $J_{\text{body}}$ , compare top panel of Fig. 2. In view of existing chemical compound this is a clear advantage.

The square, Fig. 4, performs best for ferromagnetic exchange interactions. When dipolar interactions are considered the isothermal entropy change is not as bad as for the butterfly and the chain, but not as good as for the tetrahedron.

#### IV. DISCUSSION

In this paper we investigated four typical geometric structures of four spins each as they often appear as motives in magnetic molecules. It turns out that a tetrahedral arrangement with ferromagnetic exchange interactions is most promising in view of the isothermal entropy change that is robust under the influence of dipolar interactions at sub-kelvin temperatures. Even combinations of ferromagnetic and antiferromagnetic interactions yield a reasonable magnetocaloric performance for the tetrahedron.

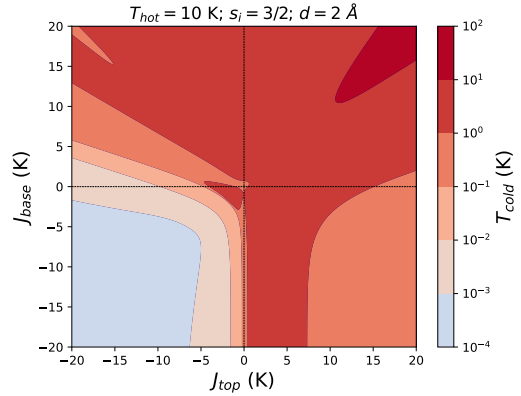


Figure 5. Adiabatic temperature change for a tetrahedron with  $s = 3/2$  with  $B_{\text{hot}} = 7$  T,  $B_{\text{cold}} = 0$ , and  $T_{\text{hot}} = 10$  K. Dipolar interactions for distances of  $d = 2$  Å are included. The magnetic field is perpendicular to the plane of the red triangle in the tetrahedron, compare Tab. I. The color map shows the respective  $T_{\text{cold}} = 0$  on a logarithmic scale.

The adiabatic temperature change is shown for a tetrahedron in Fig. 5. One notices that low temperatures can be reached for large parts of the phase diagram but not for antiferromagnetic interactions. However, strong ferromagnetic interactions lead to the best result and push the limits of magnetocaloric refrigeration to very low



temperatures (even milikelvin for the investigated scenarios). This trend is largely independent of the specific  $J_1$  and  $J_2$  [27].

In our theoretical calculations low temperatures can be achieved even in regions where the isothermal entropy change would be small, e.g., in the lower right quadrant. For a true periodic process such as a Carnot process one would of course prefer parameters that yield a not too small heat transfer per cycle, see also [24] on issues of realistic cycles.

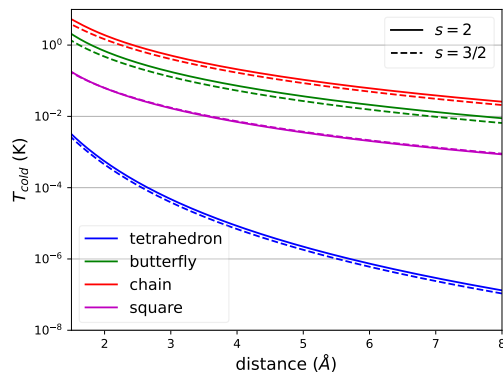


Figure 6. Adiabatic temperature change for all four investigated structures as function of the distance between spins for two spin quantum numbers;  $B_{\text{hot}} = 7$  T,  $B_{\text{cold}} = 0$ , and  $T_{\text{hot}} = 10$  K. The exchange is ferromagnetic, all  $J = -20$  K.

Finally, Fig. 6 compares the four investigated tetranuclear spin systems with ferromagnetic coupling ( $J =$

$-20$  K) in view of the adiabatic temperature change. Again,  $B_{\text{hot}} = 7$  T,  $B_{\text{cold}} = 0$ , and  $T_{\text{hot}} = 10$  K. One sees that the tetrahedron outperforms all other three structures in terms of the achievable  $T_{\text{cold}}$  for every investigated distance of spins, i.e., for every strength of the dipolar interaction. This seems to be largely independent of spin quantum number. We speculate that in the case of the tetrahedron the dipolar interaction does not split the ground multiplet as much as it does for the other three structures. The magnitude of this splitting sets the scale for the lowest achievable temperatures.

However and unfortunately, tetrahedra with larger spins – iron or gadolinium – seem to dominantly exhibit antiferromagnetic interactions, see e.g. [30–35]. Nickel-based tetrahedra may show ferromagnetic exchanges, see e.g. [36, 37] as well as some rare manganese compounds [38] do, although for nickel also antiferromagnetic couplings are reported [39]. However, the larger problem with nickel and manganese is the non-negligible single-ion anisotropy and the possible biquadratic exchange for nickel that would very likely alter the magnetocaloric behavior at sub-kelvin temperatures.

Summarizing, we think that trying to synthesize ferromagnetic tetrahedra is a worthwhile effort. This potentially includes tetrahedral chains [40, 41].

## ACKNOWLEDGMENT

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