Magnetorefrigeration capability of a gadolinium(III) coordination polymer containing trimesic acid: a correlation between the isothermal magnetic entropy change and the gadolinium content

Radovan Herchel, Kamil Kotrle and Zdeněk Trávníček*

The gadolinium(III) coordination polymer \([\text{Gd}((\text{mes})(\text{H}_2\text{O})_6\text{H}_3\text{mes})]_n\) (1), where H₃mes stands for trimesic acid, was subjected to variable temperature/field magnetizations and heat capacity measurements. Analyses of the magnetic data revealed negligible magnetic interactions \((\zeta J = -0.39 \text{ cm}^{-1})\) and the isothermal magnetic entropy change \(\Delta S_M = 36.0 \text{ J K}^{-1} \text{ kg}^{-1}\) at \(T = 2 \text{ K}\) and \(B = 9 \text{ T}\). The evaluation of the heat capacity data resulted in a similar value of \(-\Delta S_M = 34.8 \text{ J K}^{-1} \text{ kg}^{-1}\). Thus, compound 1 shows a quite large magnetocaloric effect among Gd(III)-based molecular coolants. Furthermore, the correlation of the magnetocaloric effect based on the mass concentration of Gd atoms \(c_{\text{Gd}}(\text{Gd})\) was proposed as \(-\Delta S_M = 39.5 c_{\text{Gd}}(\text{Gd})^{0.364}\) taking into account the experimental data for more than thirty Gd(III) compounds.

Results and discussion

Synthesis and crystal structure of 1

As the synthesis and the crystal structure of 1 was already reported, herein we wish only briefly to summarize the key points relevant to the reported study. The crystal structure of 1 is composed of zig-zag chains, in which the Gd(III) atoms are bridged by carboxylic groups of the mes ligand, and coordination number 9 is achieved by coordination of six molecules of water (Fig. 1). The shortest distance between Gd–Gd is 5.810 Å and the shape of the coordination polyhedron \(\{\text{GdO}_6\}\) is close to a spherical capped square antiprism according to the analysis done with the program SHAPE. Moreover, the hydrogen bonds play an important role in stabilizing the crystal structure.

Magnetic studies and DFT calculations for 1

The magnetic properties of 1 were determined in order to quantify the extent of magnetic interactions among the Gd(III) atoms (Fig. 2). The effective magnetic moment \(\mu_{\text{eff}}\) is constant almost in the whole temperature range, there is only a small decrease of \(\mu_{\text{eff}}\) when approaching \(T = 1.9 \text{ K}\), which suggests...
a very weak antiferromagnetic exchange or dipolar interactions.

The reduced isothermal magnetization (\(M_{\text{mol}}/N_A\mu_B\)) data measured at \(T = 2, 5\) and 10 K are overlapping and saturating at the maximum value of 6.9, thus magnetic anisotropy should be negligible. With the aim to fit magnetic behaviour of 1, a simple spin Hamiltonian model was used

\[
\hat{H} = \mu_B B g \hat{S}_z - zJ\langle \hat{S}_z \rangle \hat{S}_z
\]

where apart from the Zeeman term the molecular-field correction parameter \(zJ\) was introduced, which quantifies intermolecular interactions.\(^{15}\) The \(\langle \hat{S}_z \rangle\) is a thermal average of the molecular spin projection. Then, the molar magnetization can be numerically calculated as

\[
M_{\text{mol}} = -N_A \sum_i \sum_k \sum_l C_{ikl} (Z_{kl}) \exp(-\varepsilon_i/kT) / \sum_i \exp(-\varepsilon_i/kT)
\]

where \(Z\) is the matrix element of the Zeeman term and \(C\) are the eigenvectors resulting from the diagonalization of the complete spin Hamiltonian matrix. The inclusion of \(zJ\) means that iterative procedure must be applied.\(^{15}\) Both temperature and field dependent magnetic data were included in the fitting procedure, which resulted in the following set of magnetic parameters: \(zJ = -0.39\) cm\(^{-1}\), \(g = 1.98\). This means that there are almost negligible antiferromagnetic interactions among the paramagnetic Gd(III) atoms.

The magnetic exchange between the Gd(III) atoms was also studied by density functional theory (DFT), where the geometry of the molecular fragment \([\text{Gd}_2(\text{mes})_4(\text{H}_2\text{O})_{12}]^{6-}\) of 1 was extracted from the experimental X-ray structure (Fig. 3). Herein, we
utilized the well-known B3LYP functional and the $J$-values were evaluated from the energy difference $\Delta$, between the high-spin (HS) and broken-symmetry (BS) spin states

$$\Delta = E_{BS} - E_{HS}$$  \hspace{1cm} (3)

by both Ruiz’s approach

$$J_{Ruiz} = 2\Delta / [(S_1 + S_2)(S_1 + S_2 + 1)]$$  \hspace{1cm} (4)

and by Yamaguchi’s approach

$$J_{Yam} = 2\Delta / \left[ h S_2^2 \right]_{HS} - \left[ h S_2^2 \right]_{BS}$$  \hspace{1cm} (5)

Then, we obtained $\Delta = -0.227 \text{ cm}^{-1}$, which resulted in $J_{Ruiz} = -0.0081 \text{ cm}^{-1}$ and $J_{Yam} = -0.0093 \text{ cm}^{-1}$. These minute values also supported the presence of a very weak antiferromagnetic exchange in 1.

**Magnetocaloric properties of 1**

In order to evaluate the magnetocaloric effect in 1, the magnetization data were measured densely between 1.9 and 10.1 K up to maximum magnetic field of 9 T, see Fig. 4. Subsequently, we used the Maxwell equation

$$\left( \frac{dS}{dB} \right)_T = \left( \frac{dM}{dT} \right)_B$$  \hspace{1cm} (6)

to evaluate $\Delta S_M$ as

$$\Delta S_M(T_0, B) = \int_{0}^{B} \left( \frac{dM}{dT} \right)_B dB$$  \hspace{1cm} (7)

The results are depicted in Fig. 4 and the maximum value of $(-\Delta S_M)$ was found to be $36.0 \text{ J kg}^{-1} \text{ K}^{-1}$ at $T = 1.9 \text{ K}$ for highest magnetic field $B = 9 \text{ T}$.

Fig. 4  (a) The densely-measured magnetization data of 1; (b) the isothermal magnetic entropy change $\Delta S_M$ of 1 calculated from the magnetization data using the eqn (7); (c) the mass heat capacity of 1 measured at various magnetic fields up to 9 T; (d) the isothermal magnetic entropy change $\Delta S_M$ of 1 calculated from the heat capacity data using the eqn (9).
Next, the heat capacity of 1 was also measured at different magnetic fields in the temperature interval between 1.9 and 100 K in order to evaluate the magnetocaloric effect of this compound with a different technique, see Fig. 4. The entropy at a given magnetic field is usually calculated as

$$S(T_0, B) = \int_0^{T_0} \frac{C(T, B)}{T} \, dT \quad \text{(8)}$$

The right utilization of this equation ultimately requires knowledge of the temperature dependence of specific heat (C) down to absolute zero. This dependence is not known due to the limitation of our hardware ($T_{\text{min}} = 1.9$ K), and thus the different approach was used, which was theoretically discussed in ref. 10 and applied e.g. in ref. 17 and 18. More specifically, every magnetic system at a given field $B_0$ is characterized by a temperature $T_{\text{Int}}$ above which total specific heats studied from 0 to $B_0$ coincide. Thus, above $T_{\text{Int}}$, the magnetic entropy is already saturated and temperature independent. Considering this fact, the eqn (8) can be modified and $\Delta S_M$ can be calculated as follows

$$\Delta S_M(T_0, \Delta B) = \int_{T_0}^{T_{\text{Int}}} \frac{C(T, B_0)}{T} \, dT - \int_{T_0}^{T_{\text{Int}}} \frac{C(T, B_1)}{T} \, dT \quad \text{(9)}$$

where $C(T_0, B_0)$ and $C(T_1, B_1)$ are experimental heat capacities for given temperature $T$ and zero magnetic field $B_0$ and non-zero magnetic field $B_1$, respectively. It is obvious that maximum $-\Delta S_M = 34.8$ J kg$^{-1}$ K$^{-1}$ is achieved at $T = 1.9$ K for highest magnetic field and this value is similar to that obtained from magnetization data.
The correlation of the isothermal magnetic entropy change $\Delta S_M$ of the Gd(III) compounds based either on $M_r/N$(Gd) ratios (top) or on the mass concentration $c_m$(Gd) (bottom). The full points are experimental data listed in Table 1 and full lines are calculated with the eqn (10) and (11), respectively.

To sum up, the value of $-\Delta S_M = 36.0$ J K$^{-1}$ kg$^{-1}$ at $T = 2$ K and $B = 9$ T for 1 is comparable with other gadolinium-based compounds containing either inorganic or organic acids as ligands, see Table 1.

**Magnetocaloric effect in Gd(m) compounds**

In general, it is well-known that magnetocaloric properties of the paramagnetic coordination compounds are dependent on the content of the central metal atoms, however, there exists no quantitative relationship which could be used to correlate $\Delta S_M$ with the content of Gd. Only recently, it was proposed that $\Delta S_M$ could correlate with the ratio of $M_r/N$(Gd) for Gd(m) complexes based on organic carboxylates, however, no quantitative relationship was given.

Therefore, we collected the information about Gd(m) compounds containing inorganic/organic acids for which the magnetocaloric effect was studied (Table 1). Evidently, $-\Delta S_M$ values are increasing with increasing ratio of $M_r/N$(Gd) and dependence is not linear. Therefore, we proposed the following quantitative relationship for $\Delta S_M$ as

$$-\Delta S_M = 8914(M_r/N$(Gd))$^{-0.913}\quad (10)$$

However, this relationship does not take into account the density of the materials. Thus, we also suggested another correlation, in which the mass concentration of Gd atoms is utilized. The mass concentration $c_m$(Gd) is proportional to the mass fraction of Gd ($w_{Gd}$) and density of crystals ($\rho$), therefore it holds $c_m$(Gd) = $w_{Gd}$/$\rho$. Then, the following correlations was found

$$-\Delta S_M = 39.5c_m$(Gd)$^{0.364}\quad (11)$$

The correlations outlined in the eqn (10) and (11) are depicted in Fig. 5. We presume that the observed scattering of the experimental data around the proposed correlation functions is due to the small variation of the magnetic exchange and/or magnetic anisotropy of the Gd(m) ions in these compounds. Nevertheless, these correlations can be used to simply estimate magnetocaloric effect for newly prepared Gd(m) compounds.

**Conclusions**

To conclude, the magnetic and magnetocaloric properties of [Gd(mes)(H$_2$O)$_6$]$_n$ (1) were investigated and revealed a very weak antiferromagnetic interactions ($z_f = -0.39$ cm$^{-1}$), with $-\Delta S_M$ equals $36.0$ J K$^{-1}$ kg$^{-1}$ at $T = 2$ K and $B = 9$ T. This value is higher than that of $29.0$ J K$^{-1}$ kg$^{-1}$ found for [Gd$_2$(N-BDC)$_3$(dmf)$_3$]$_n$ (N-BDC = 2-amino-1,4-benzedicarboxylic acid), the next one only compound containing solely aromatic polycarboxylic acids as bridging ligands. This comparison is in agreement with our suggested correlation based on the mass concentration, because $c_m$(Gd) = 0.83 for 1 is larger than $c_m$(Gd) = 0.39 for [Gd$_2$(N-BDC)$_3$(dmf)$_3$]$_n$. Thus, this work revealed a large magnetocaloric effect for 1 and proposed two general quantitative correlations for the evaluation of the magnetocaloric effect of Gd(m) coordination compounds comprising organic and/or inorganic acids as ligands.

**Experimental section**

**Synthesis**

All the reagents and solvents were purchased from commercial sources and used as received. The polymeric compound [Gd(mes)(H$_2$O)$_6$]$_n$ (1) was prepared according to the previously reported literature procedure. The purity and composition of the compound (1) was analysed by elemental analysis, FTIR and powder X-ray diffraction (PXRD).

Anal. calcd for Gd$_4$C$_9$H$_{14}$O$_{12}$ ($M_r = 472.5$) (%), C, 22.88, H, 3.20, found: C, 22.88, H, 2.88. FTIR (cm$^{-1}$): $v$(O–H) = 3478 (s), 3403 (s), 3336 (s), 8253 (s), $v$(C–H)$_{arom}$ = 3092 (m), $v$(C–O) and $v$(C–C)$_{arom}$ = 1608 (s), 1549 (s), 1432 (s), 1367 (s).
**Physical methods.** Elemental analysis (C, H) was performed on a Flash 2000 CHNO-S Analyser (Thermo Scientific). Infrared (IR) spectra of the complexes were recorded on a Thermo Nicolet NEXUS 670 FT-IR spectrometer (Thermo Nicolet) employing the ATR technique on a diamond plate in the range of 400–4000 cm⁻¹. Temperature dependence of the magnetization at \( B = 0.1 \) T from 1.9 to 300 K and the isothermal magnetizations at \( T = 2, 5 \) and 10 K up to \( B = 9 \) T were measured using PPMS Dynacool VSM magnetometer (Quantum Design). Further magnetic data were collected in the temperature range from 1.9 to 10.1 K with step equal 0.2 K for magnetic fields from 0 to 9 T with step 0.25 T and subsequently used for the calculation of the magnetic entropy change. The heat capacity was measured on a PPMS Dynacool using a relaxation method in the temperature interval of 1.9–100 K and magnetic field up to 9 T. The X-ray powder diffraction pattern was recorded on an MiniFlex600 (Rigaku) instrument equipped with the Bragg–Brentano geometry, and with nickel-filtered Cu Kα,1,2 radiation.

**Theoretical methods.** The DFT calculations were performed using the ORCA 3.0.3 computational package. The relativistic effects were included in all the calculations using the scalar relativistic contracted version of the def2-TZVPP basis functions and with the zero-order regular approximation (ZORA). The single point energy calculations were based on the molecular geometry derived from experimental X-ray data (Cambridge Structural Database (CSD)) code RAVJUV) utilizing the B3LYP functional. The isotropic exchange constant \( J \) was calculated by comparing the energies of high-spin (HS) and broken-symmetry (BS) spin states utilizing both Ruiz’s approach and Yamaguchi’s approach. The figure showing structural motif was done with Diamond software and spin density plot with VESTA 3 software.

**Acknowledgements**

We acknowledge the financial support from the National Programme of Sustainability I (LOI1305) of the Ministry of Education, Youth and Sports of the Czech Republic, and from Palacký University in Olomouc (PrF_2016_007 and PrF_2017_018). We also thank prof. Martin Orendáč from Pavel Jozef Safářík University in Košice for helpful discussions concerning the magnetocaloric effect.

**Notes and references**

1 Luminescence of lanthanide ions in coordination compounds and nanomaterials, ed. A. de Bettencourt-Dias, Wiley, 2014.
2 R. A. Layfield and M. Murugesu, Lanthanides and Actinides in Molecular Magnetism, Wiley, 2015.
3 Z. Zhou and Z.-R. Lu, *Wiley Interdiscip. Rev.: Nanomed. Nanobiotecnol.*, 2013, 5, 1.
4 K. W.-Y. Chan and W.-T. Wong, *Coord. Chem. Rev.*, 2007, 251, 2428.
5 I. S. Yu, A. K. Zvezdin, S. P. Gubin, A. S. Mischenko and A. M. Tishin, *J. Phys. D: Appl. Phys.*, 2001, 34, 1162.
6 J. W. Sharples and D. Collison, *Polyhedron*, 2013, 54, 91.
7 J. W. Sharples, Y.-Z. Zheng, F. Tuna, E. J. L. McInnes and D. Collison, *Chem. Commun.*, 2011, 47, 7650.
8 F. S. Guo, J. D. Leng, J. L. Liu, Z. S. Meng and M. L. Tong, *Inorg. Chem.*, 2012, 51, 405.
9 J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios and M. Evangelisti, *Nat. Commun.*, 2014, 5, 5321.
10 J.-L. Liu, Y.-C. Chen, F.-S. Guo and M.-L. Tong, *Coord. Chem. Rev.*, 2014, 281, 26.
11 R. Sibille, T. Mazet, B. Malaman and M. François, *Chem.– Eur. J.*, 2012, 18, 12970.
12 G. Lorusso, M. A. Palacios, G. S. Nichol, E. K. Brechin, O. Roubau and M. Evangelisti, *Chem. Commun.*, 2012, 48, 7592.
13 K. Davies, S. A. Bourne and C. L. Oliver, *Cryst. Growth Des.*, 2012, 12, 1999.
14 M. Pinsky and D. Avnir, *Inorg. Chem.*, 1998, 37, 5575.
15 R. Boča, *Theoretical Foundations of Molecular Magnetism*, Elsevier, 1999.
16 A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and its Applications*, IOP Publishing Ltd, 2003.
17 Y. Meng, Y.-C. Chen, Z.-M. Zhang, Z.-J. Lin and M.-L. Tong, *Inorg. Chem.*, 2014, 53, 9052.
18 J.-Z. Qiu, L.-F. Wang, Y.-C. Chen, Z.-M. Zhang, Q.-W. Li and M.-L. Tong, *Chem.– Eur. J.*, 2016, 22, 802.
19 Y.-C. Chen, J. Prokleska, W.-J. Xu, J.-L. Liu, J. Liu, W.-X. Zhang, J.-H. Jia, V. Sechovsky and M.-L. Tong, *J. Mater. Chem. C*, 2015, 3, 12206.
20 Y.-C. Chen, L. Qin, Z.-S. Meng, D.-F. Yang, C. Wu, Z. Fu, Y.-Z. Zheng, J.-L. Liu, R. Tarasenko, M. Orendac, J. Prokleska, V. Sechovsky and M.-L. Tong, *J. Mater. Chem. A*, 2014, 2, 9851.
21 E. Palacios, J. A. Rodríguez-Velamazán, M. Evangelisti, G. J. McIntyre, G. Lorusso, D. Visser, L. J. de Jongh and L. A. Boatner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2014, 90, 214423.
22 Y. Yang, Q.-C. Zhang, Y.-Y. Pan, L.-S. Long and L.-S. Zheng, *Chem. Commun.*, 2015, 51, 7317.
23 Y. Wang, L. Qin, G.-J. Zhou, X. Ye, J. He and Y.-Z. Zheng, *J. Mater. Chem. C*, 2016, 4, 6473.
24 G. Lorusso, J. W. Sharples, E. Palacios, O. Roubau, E. K. Brechin, R. Sessoli, A. Rossin, F. Tuna, E. J. L. McInnes, D. Collison and M. Evangelisti, *Adv. Mater.*, 2013, 25, 4653.
25 S.-D. Han, X.-H. Miao, S.-J. Liu and X.-H. Bu, *Inorg. Chem. Front.*, 2014, 1, 549.
26 Y.-C. Chen, F.-S. Guo, Y.-Z. Zheng, J.-L. Liu, J.-D. Leng, R. Tarasenko, M. Orendáč, J. Prokleska, V. Sechovsky and M.-L. Tong, *Chem.–Eur. J.*, 2013, 19, 13504.
27 F.-S. Guo, J.-D. Leng, J.-L. Liu, Z.-S. Meng and M.-L. Tong, *Inorg. Chem.*, 2012, 51, 405.
28 S. Biswas, A. Adhikary, S. Goswami and S. Konar, *Dalton Trans.*, 2013, 42, 13331.
29 Y.-L. Hou, G. Xiong, P.-F. Shi, R.-R. Cheng, J.-Z. Cui and B. Zhao, *Chem. Commun.*, 2013, 49, 6066.
30 L.-X. Chang, G. Xiong, L. Wang, P. Cheng and B. Zhao, *Chem. Commun.*, 2013, 49, 1055.
31 F.-S. Guo, Y.-C. Chen, L.-L. Mao, W.-Q. Lin, J.-D. Leng, R. Tarasenko, M. Orendáč, J. Prokleška, V. Sechovský and M.-L. Tong, Chem.–Eur. J., 2013, 19, 14876.
32 S.-J. Liu, C. Cao, C.-C. Xie, T.-F. Zheng, X.-L. Tong, J.-S. Liao, J.-L. Chen, H.-R. Wen, Z. Chang and X.-H. Bu, Dalton Trans., 2016, 45, 9209.
33 M. Evangelisti, O. Roubeau, E. Palacios, A. Camón, T. N. Hooper, E. K. Brechin and J. J. Alonso, Angew. Chem., Int. Ed., 2011, 50, 6606.
34 J.-M. Jia, S.-J. Liu, Y. Cui, S.-D. Han, T.-L. Hu and X.-H. Bu, Cryst. Growth Des., 2013, 13, 4631.
35 M. Wu, F. Jiang, X. Kong, D. Yuan, L. Long, S. A. Al-Thabaiti and M. Hong, Chem. Sci., 2013, 4, 3104.
36 Y. Zheng, Q.-C. Zhang, L.-S. Long, R.-B. Huang, A. Muller, J. Schnack, L.-S. Zheng and Z. Zheng, Chem. Commun., 2013, 49, 36.
37 K. H. Zangana, E. M. Pineda, J. Schnack and R. E. P. Winpenny, Dalton Trans., 2013, 42, 14045.
38 S.-J. Liu, J.-P. Zhao, J. Tao, J.-M. Jia, S.-D. Han, Y. Li, Y.-C. Chen and X.-H. Bu, Inorg. Chem., 2013, 52, 9163.
39 S. Goswami, A. Adhikary, H. S. Jena and S. Konar, Dalton Trans., 2013, 42, 9813.
40 J. A. Sheikh, A. Adhikary and S. Konar, New J. Chem., 2014, 38, 3006.
41 L. Sedláková, J. Hanko, A. Orendáčová, M. Orendáč, C. L. Zhou, W. H. Zhu, B. W. Wang, Z. M. Wang and S. Gao, J. Alloys Compd., 2009, 487, 425.
42 F. Neese, Wiley Interdiscip. Rev.: Comput. Mol. Sci., 2012, 2, 73.
43 D. A. Pantazis, X.-Y. Chen, C. R. Landis and F. Neese, J. Chem. Theory Comput., 2008, 4, 908.
44 E. Vanlenthe, E. J. Baerends and J. G. Snijders, J. Chem. Phys., 1993, 99, 4597.
45 C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater., 2016, 72, 171.
46 C. T. Lee, W. T. Yang and R. G. Parr, Phys. Rev. B: Condens. Matter Mater. Phys., 1988, 37, 785.
47 A. D. Becke, J. Chem. Phys., 1993, 99, 5648.
48 P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, J. Phys. Chem., 1994, 98, 11623.
49 E. Ruiz, J. Cano, S. Alvarez and P. Alemany, J. Comput. Chem., 1999, 20, 1391.
50 T. Soda, Y. Kitagawa, T. Onishi, Y. Takano, Y. Shigeta, H. Nagao, Y. Yoshioka and K. Yamaguchi, Chem. Phys. Lett., 2000, 319, 223.
51 H. Putz and K. Brandenburg, Diamond – Crystal and Molecular Structure Visualization, version 4.3, Crystal Impact GbR: Bonn, Germany, 2016.
52 K. Momma and F. Izumi, J. Appl. Crystallogr., 2011, 44, 1272.