RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2017, **7**, 30763

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 *

Received 2nd May 2017
Accepted 1st June 2017

DOI: 10.1039/c7ra04945e

rsc.li/rsc-advances

The Gd(III) coordination polymer $[Gd(mes)(H_2O)_6]_n$ (**1**), where H_3mes stands for trimesic acid, was subjected to variable temperature/field magnetizations and heat capacity measurements. Analyses of the magnetic data revealed negligible magnetic interactions ($zJ = -0.39$ cm^{-1}) and the isothermal magnetic entropy change $-\Delta S_M = 36.0$ J K^{-1} kg^{-1} at $T = 2$ K and $B = 9$ T. The evaluation of the heat capacity data resulted in a similar value of $-\Delta S_M = 34.8$ J K^{-1} 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_m(Gd)) was proposed as $-\Delta S_M = 39.5c_m(Gd)^{0.364}$ taking into account the experimental data for more than thirty Gd(III) compounds.

Introduction

The coordination compounds of lanthanides are of great interest due to their fascinating luminescent[1] and magnetic properties.[2] The gadolinium(III) compounds themselves are attention-grabbing from the application point of view due to the fact that they can be utilized as MRI agents[3,4] and also as magnetic coolants. Indeed, the paramagnetic compounds with a large spin are prospective materials for magnetic refrigeration at low temperatures based on the magnetocaloric effect.[5,6] The coordination compounds of Gd(III) began to be explored as magnetic coolants quite recently, and both polynuclear coordination compounds (molecular clusters)[7] and polymeric coordination compounds[8] were studied. Interestingly, a heptanuclear Gd(III) compound $[Gd_7(OH)_6(thmeH_2)_5(thmeH)(tpa)_6(CH_3CN)_2](NO_3)_2$, where H_3thme = tris(hydroxymethyl)ethane and Htpa = triphenylacetic acid, was shown to act as an efficient magnetic coolant, with $T = 200$ mK obtained using an adiabatic demagnetization experiment.[9] The efficiency of such materials is usually determined by the isothermal magnetic entropy change ΔS_M.[10] Up to now, there are several reports on Gd(III) polymeric coordination compounds containing aromatic carboxylic acids as ligands and revealing the large magnetocaloric effect, *e.g.* $[Gd(HCOO)(bdc)]_n$ (bdc = 1,4-benzenedicarboxylic acid) with $-\Delta S_M = 47.0$ J K^{-1} kg^{-1},[11] and $[Gd_2(N\text{-BDC})_3(dmf)_4]_n$ (*N*-BDC = 2-amino-1,4-benzenedicarboxylic acid) with $-\Delta S_M = 29.0$ J K^{-1} kg^{-1}.[12] This motivated us to investigate magnetic properties of the recently reported[13] polymeric compound $[Gd(mes)(H_2O)_6]_n$ (**1**) comprising 1,3,5-benzenetricarboxylic acid (trimesic acid, H_3mes) as a bridging ligand. Thus, we report on magnetic and magnetocaloric properties of this compound studied both experimentally and theoretically. Furthermore, a general correlation between the magnetorefrigeration capabilities and the gadolinium content of Gd(III) compounds is proposed.

Department of Inorganic Chemistry, Regional Centre of Advanced Technologies and Materials, Faculty of Science, Palacký University, 17. listopadu 12, CZ-771 46 Olomouc, Czech Republic. E-mail: zdenek.travnicek@upol.cz

Results and discussion

Synthesis and crystal structure of 1

As the synthesis and the crystal structure of **1** was already reported,[13] 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).[13]

The shortest distance between Gd···Gd is 5.810 Å and the shape of the coordination polyhedron $\{GdO_9\}$ is close to a spherical capped square antiprism according to the analysis done with the program SHAPE.[14] 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 μ_{eff} is constant almost in the whole temperature range, there is only a small decrease of μ_{eff} when approaching $T = 1.9$ K, which suggests

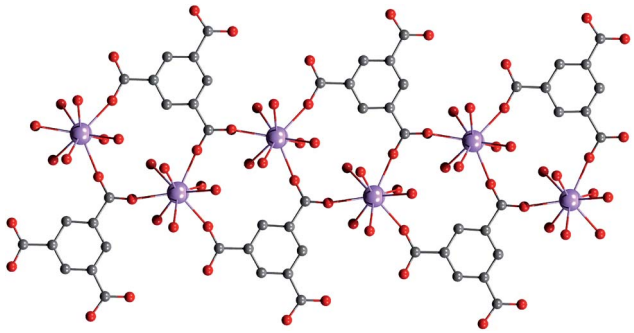

Fig. 1 Part of the crystal structure of **1** showing a zig–zag chain motif of the Gd(III) atoms.[13] The hydrogen atoms were omitted for clarity.

a very weak antiferromagnetic exchange or dipolar interactions. The reduced isothermal magnetization ($M_{mol}/N_A\mu_B$) 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

$$\hat{H} = \mu_B B g \hat{S}_z - zJ\langle\hat{S}_z\rangle\hat{S}_z \quad (1)$$

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

$$M_{mol} = -N_A \frac{\sum_i \left(\sum_k \sum_l C^+_{ik}(Z)_{kl} C_{li} \right) \exp(-\varepsilon_i/kT)}{\sum_i \exp(-\varepsilon_i/kT)} \quad (2)$$

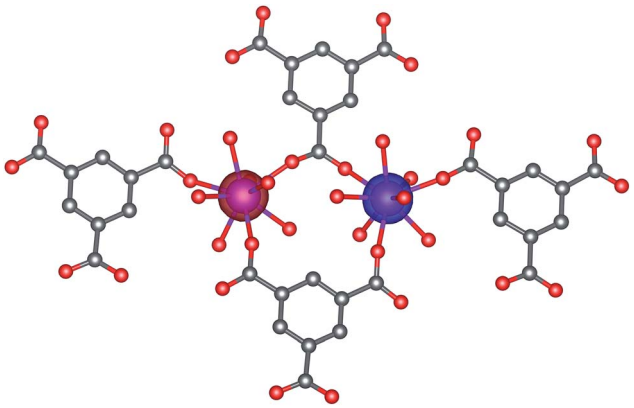

Fig. 3 The calculated isodensity surfaces of the broken symmetry spin states using B3LYP/def2-TZVPP for the molecular fragment $[Gd_2(mes)_4(H_2O)_{12}]^{6-}$ of **1**. The positive and negative spin densities are represented by blue, and red surfaces, respectively, with the cut-off values of 0.01 e bohr^{-3}. Hydrogen atoms are omitted for clarity.

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 $[Gd_2(mes)_4(H_2O)_{12}]^{6-}$ was extracted from the experimental X-ray structure (Fig. 3). Herein, we

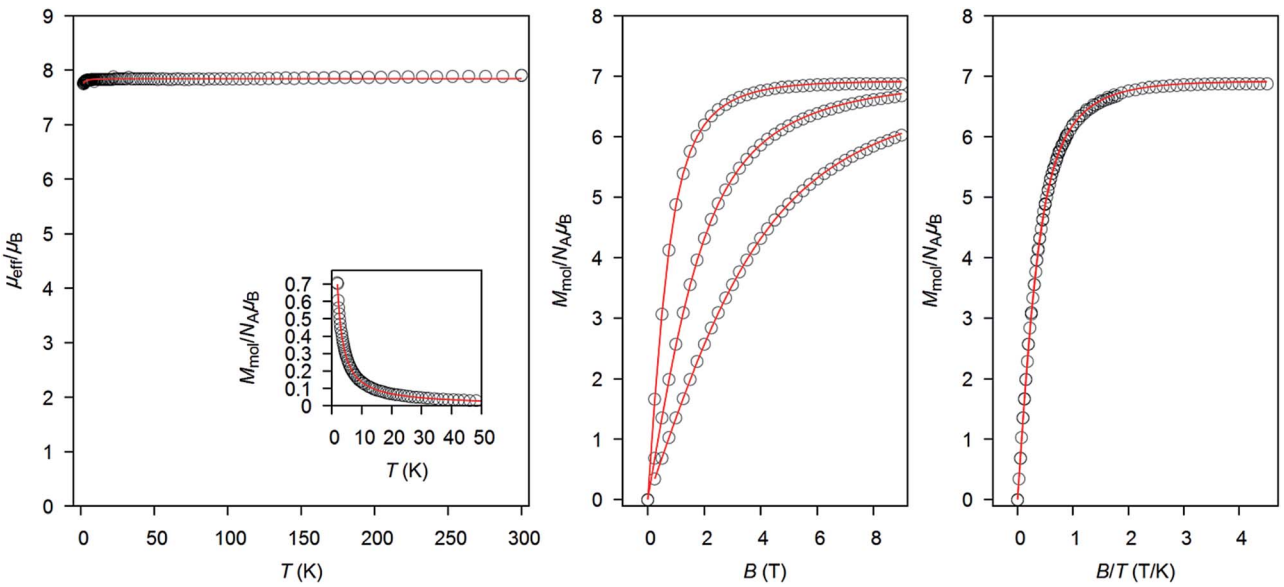

Fig. 2 The magnetic data for **1**. (Left) The temperature dependence of the effective magnetic moment and molar magnetization measured at $B = 0.1$ T. (Middle) The isothermal magnetization data measured at $T = 2$, 5 and 10 K. (Right) The reduced magnetization data measured at $T = 2$, 5 and 10 K. Open circles: experimental data and red solid lines calculated data using the eqn (1), with $zJ = -0.39$ cm^{-1}, $g = 1.98$.

utilized the well-known B3LYP functional and the J-values were evaluated from the energy difference Δ, between the high-spin (HS) and broken-symmetry (BS) spin states

$$\Delta = E_{BS} - E_{HS} \quad (3)$$

by both Ruiz's approach

$$J^{Ruiz} = 2\Delta/[(S_1 + S_2)(S_1 + S_2 + 1)] \quad (4)$$

and by Yamaguchi's approach

$$J^{Yam} = 2\Delta/[\langle S^2\rangle_{HS} - \langle S^2\rangle_{BS}] \quad (5)$$

Then, we obtained $\Delta = -0.227\ cm^{-1}$, which resulted in $J^{Ruiz} = -0.0081\ cm^{-1}$ and $J^{Yam} = -0.0093\ cm^{-1}$. 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[16]

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

to evaluate ΔS_M as

$$\Delta S_M(T_0, B) = \int_0^B \left(\frac{dM}{dT}\right)_B dB \quad (7)$$

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

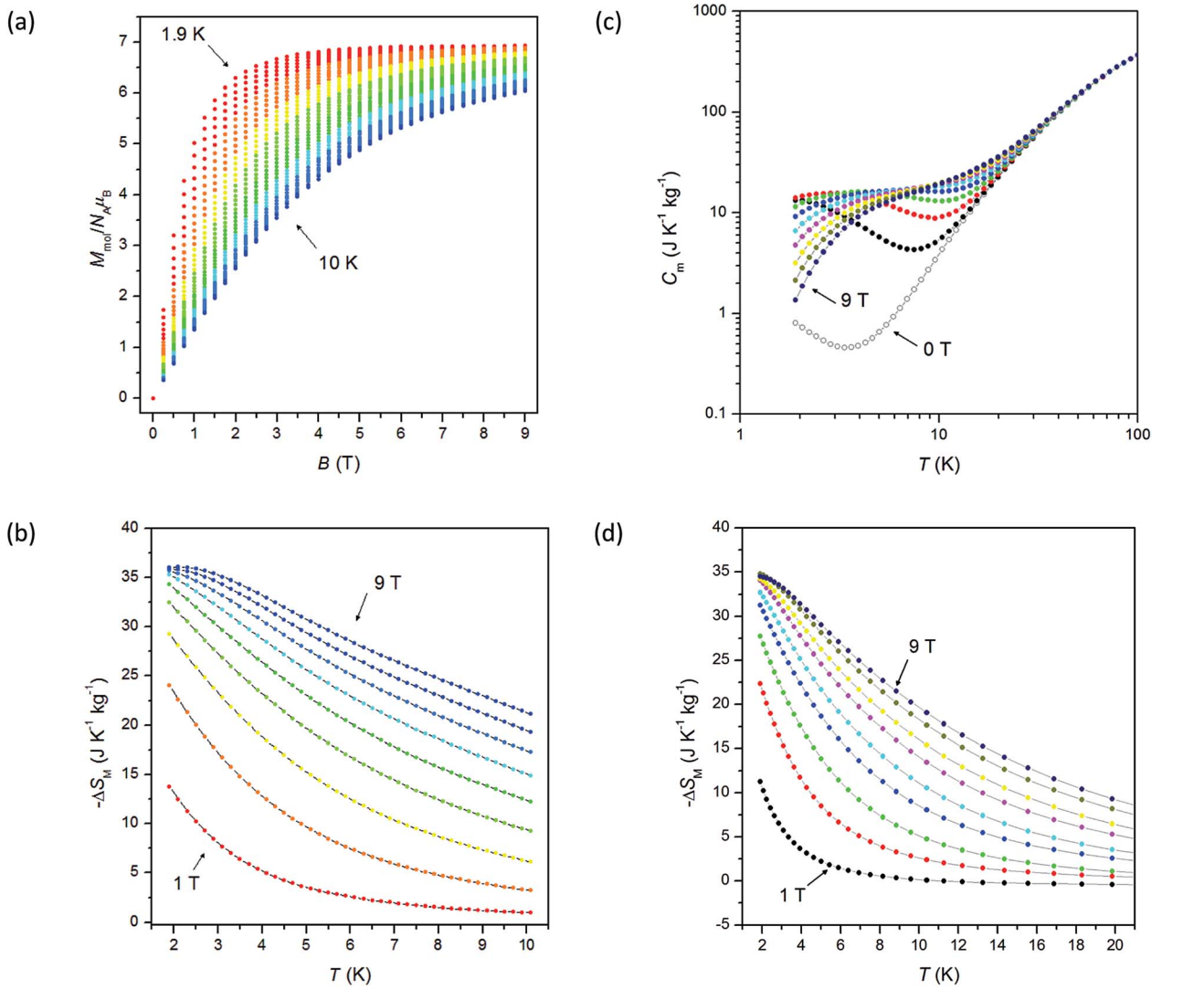

Fig. 4 (a) The densely-measured magnetization data of **1**; (b) the isothermal magnetic entropy change ΔS_M of **1** calculated from the magnetization data using the eqn (7); (c) the mass heat capacity of **1** measured at various magnetic fields up to 9 T; (d) the isothermal magnetic entropy change ΔS_M of **1** calculated from the heat capacity data using the eqn (9).

Table 1 The isothermal magnetic entropy changes $-\Delta S_M$ in Gd(III) compounds containing inorganic and/or organic acids as ligands[a]

Compound[b]	$-\Delta S_M$ (J kg^{-1} K^{-1})	T (K)	ΔB (T)	M/N(Gd)	ρ (g cm^{-3})	w_{Gd} (%)	Ref.
GdF_3	74.8	3.2	9	214.24	7.062	73.39	19
$[Gd(OH)CO_3]_n$	66.4	1.8	7	234.27	5.349	67.12	20
$GdPO_4$	62.0	2.1	7	252.22	5.99	62.34	21
$Gd(OH)_3$	62.0	2	7	208.27	3.670	75.5	22
$[Gd(OH)_2Cl]n$	61.8	3	7	226.72	5.161	69.36	23
$[Gd_3(OH)_8Cl]_n$	59.8	3	7	214.42	5.181	73.34	23
$[Gd(HCOO)_3]_n$	55.9	1.8	7	292.30	3.856	53.80	24
$[Gd_4(SO_4)_4(\mu_3\text{-}OH)_4(H_2O)]_n$	51.3	2	7	274.82	3.877	57.22	25
$[Gd_6(OH)_6(suc)_5(H_2O)_2]_n\cdot 4nH_2O$	48.0	1.8	7	317.35	2.99	53.37	26
$[Gd(OAc)_3(H_2O)_{0.5}]_n$	47.7	1.8	7	343.39	2.228	45.79	27
$[Gd(C_4O_4)(OH)(H_2O)_4]_n$	47.3	3	9	358.36	2.383	43.88	28
$[Gd(HCOO)(bdc)]_n$	47.0	2.25	9	366.38	2.662	42.92	11
$\{[Gd_6O(OH)_8(ClO_4)_4(H_2O)_6](OH)_4\}_n$	46.6	2.5	7	278.25	4.627	56.51	29
$[Gd_{24}(DMC)_{36}(CO_3)_{18}(H_2O)_2]\cdot 6H_2O$	46.1	2.5	7	340.39	1.951	46.20	30
$[Gd(HCOO)(OAc)_2(H_2O)_2]_n$	45.9	1.8	7	356.39	2.397	44.12	12
$[Gd(OAc)_3(MeOH)]_n$	45.0	1.8	7	363.40	2.149	42.92	27
$[Gd_{48}O_6(OH)_{84}(CAA)_{36}(NO_3)_6(H_2O)_{24}(EtOH)_{12}(NO_3)Cl_2]Cl_3\cdot 6DMF\cdot 5EtOH\cdot 20H_2O$	43.6	1.8	7	313.83	2.769	50.11	31
$[Gd_2(OH)_2(suc)_2(H_2O)]_n\cdot 2nH_2O$	42.8	2.6	7	317.35	2.815	49.55	26
$[Gd(nta)(H_2O)_2]_n$	42.0	2	7	363.38	2.690	43.27	32
$[Gd(cit)(H_2O)]_n$	41.5	2	7	363.36	2.985	43.28	32
$[\{Gd(OAc)_3(H_2O)_2\}_2]\cdot 4H_2O$	40.6	1.8	7	406.44	2.038	38.69	33
$\{[Gd_2(IDA)_3]\cdot 2H_2O\}_n$	40.6	2	7	371.90	2.480	42.28	34
$[Gd_{36}O_6(OH)_{49}(NA)_{36}(NO_3)_6(N_3)_3(H_2O)_{20}]_nCl_{2n}\cdot 28nH_2O$	39.7	2.5	7	344.99	2.303	45.58	35
$[Gd_{38}O(OH)_{42}(ClO_4)_6(CAA)_{37}(H_2O)_{36}(EtOH)_6](ClO_4)_{10}(OH)_{17}\cdot 14DMSO\cdot 13H_2O$	37.9	1.8	7	376.27	2.689	41.86	31
$[Gd(mes)(H_2O)_6]_n$ (**1**)	36.0	1.9	9	472.46	2.484	33.28	This work
$[Gd_{12}Mo_4O_{16}(Hdhpimp)_6(OH)_4(OAc)_{12}]\cdot 12MeOH\cdot 8H_2O$	35.3	3	7	415.93	2.181	37.27	36
$[Gd_8(O_3P^tBu)_6(OH)_2(H_2O)_2(HO^iBu)(O_2C^tBu)_{12}](NH_3{}^iPr)_2$	32.3	3	7	443.67	1.394	35.44	37
$[Gd_{10}(3\text{-}TCA)_{22}(\mu_3\text{-}OH)_8(H_2O)_4]$	31.2	3	7	457.77	2.205	34.35	38
$[GdNa(C_5O_5)_2(H_2O)_7]_n$	31.0	3	7	586.44	2.359	27.28	39
$[Gd_2(N\text{-}BDC)_3(dmf)_4]_n$	29.0	1.8	7	452.14	1.421	27.48	12
$[Gd_4(\mu_3\text{-}OH)_2(bbam)_2(abam)(tttt)(HOCH_3)_2]\cdot 11H_2O$	27.2	3	7	632.19	1.506	24.87	40
$[Gd_7(OH)_6(thmeH_2)_5(thmeH)(tpa)_6(MeCN)_2](NO_3)_2$	23.0	3	7	549.10	1.797	28.64	7
$[Gd_2(fum)_3(H_2O)_4]_n\cdot 3nH_2O$	20.7	1.2	5	391.39	2.515	40.17	41

[a] M_r/N(Gd) is relative molecular mass divided by the number of Gd atoms; ρ – calculated density obtained from X-ray structural data; w_{Gd} – mass fraction. [b] Abbreviations for ligands: Suc = succinate; Bdc = 1,4-benzenedicarboxylic acid; DMC = *N*,*N*-dimethylcarbamic acid; CAA = chloroacetic acid; nta = nitrilotriacetic acid; cit = citric acid; IDA = iminodiacetic acid; NA = nicotinic acid; Tacn = *N*,*N*′,*N*″-trimethyl-1,4,7-triaza-cyclononane; Dhpimp = (*E*)-2-(2,3-dihydroxypropylimino)methyl)-phenol; H_3mes = 1,3,5-benzenetricarboxylic acid; Tea = triethanolamine; TCA = thiophene-3-carboxylic acid; *N*-BDC = 2-amino-1,4-benzenedicarboxylic acid; Bbam = 3-bis((*E*)-(2-hydroxy-3-methoxybenzylidene)amino)maleonitrile; Abam = 2-amino-3-((*E*)-(2-hydroxy-3-methoxy benzylidene)amino)maleonitrile; Tttt = (1*E*,3*Z*,8*Z*,10*E*)-1,6,11-tris(2-hydroxy-3-methoxyphenyl)-2,5,7,10-tetraazaundeca-1,3,8,10-tetraene-3,4,8,9-tetracarbonitrile; Bipy = bipyridine; Thme = tris(hydroxymethyl)ethane; Tpa = triphenylacetic acid; Fum = fumarate; L = *N*,*N*′,*N*″-trimethyl-*N*,*N*″-bis(2-hydroxy-3-methoxy-5-methylbenzyl)-diethylenetriamine; Bmd = *N*,*N*′-bis(3-methoxysalicylidene)-1,3-diaminobenzene; Pmpm = phenol-2-methoxy-6-[(*E*)-(phenylimino)methyl].

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 given magnetic field is usually calculated as

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

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 ($T_{min} = 1.9$ 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_{HT} above which total specific heats studied from 0 to B_0 coincide. Thus, above T_{HT} the magnetic entropy is already saturated and temperature independent. Considering this fact, the eqn (8) can be modified and ΔS_M can be calculated as follows

$$\Delta S_M(T_0, \Delta B) = \int_{T_0}^{T_{HT}} \frac{C(T, B_0)}{T}\,\mathrm{d}T - \int_{T_0}^{T_{HT}} \frac{C(T, B_1)}{T}\,\mathrm{d}T \quad (9)$$

where $C(T,B_0)$ and $C(T,B_1)$ 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.

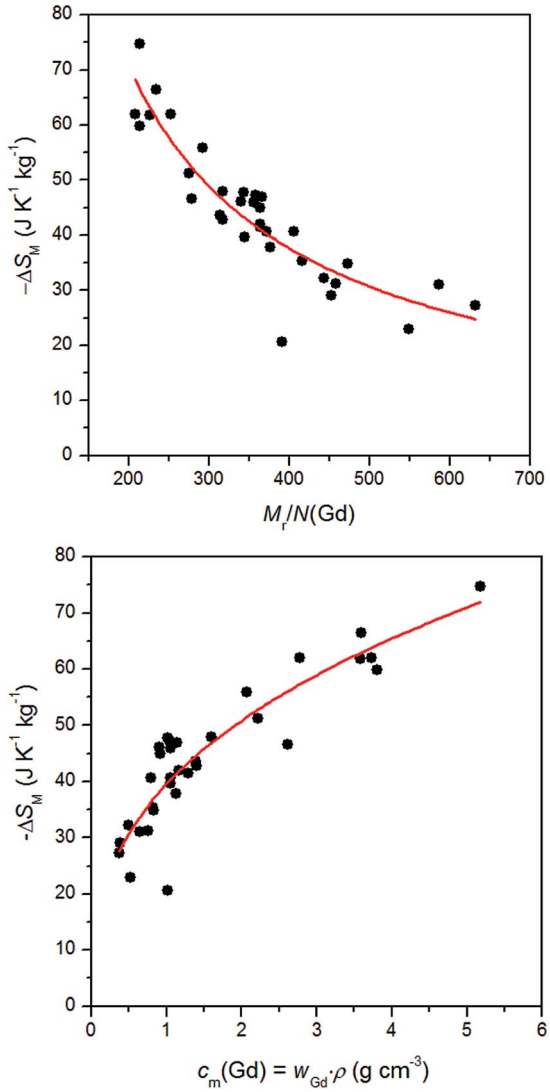

Fig. 5 The correlation of the isothermal magnetic entropy change ΔS_M of the Gd(III) compounds based either on M_r/N(Gd) ratios (top) or on the mass concentration c_m(Gd) (bottom). The full points are experimental data listed in Table 1 and full lines are calculated with the eqn (10) and (11), respectively.

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(III) 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 ΔS_M with the content of Gd. Only recently, it was proposed that ΔS_M could correlate with the ratio of M_r/N(Gd) for Gd(III) complexes based on organic carboxylates, however, no quantitative relationship was given.[32] Therefore, we collected the information about Gd(III) 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 ΔS_M as

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

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 (ρ), therefore it holds $c_m(\mathrm{Gd}) = w_{Gd}\rho$. Then, the following correlations was found

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

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(III) ions in these compounds. Nevertheless, these correlations can be used to simply estimate magnetocaloric effect for newly prepared Gd(III) compounds.

Conclusions

To conclude, the magnetic and magnetocaloric properties of $[Gd(mes)(H_2O)_6]_n$ (**1**) were investigated and revealed a very weak antiferromagnetic interactions ($zJ = -0.39$ 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 $[Gd_2(N\text{-BDC})_3(dmf)_4]_n$ (N-BDC = 2-amino-1,4-benzenedicarboxylic 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 $c_m(\mathrm{Gd}) = 0.83$ for **1** is larger than $c_m(\mathrm{Gd}) = 0.39$ for $[Gd_2(N\text{-BDC})_3(dmf)_4]_n$. 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(III) 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 $[Gd(mes)(H_2O)_6]_n$ (**1**) was prepared according to the previously reported literature procedure.[13] The purity and composition of the compound (**1**) was analysed by elemental analysis, FTIR and powder X-ray diffraction (PXRD).

Anal. calcd for $Gd_1C_9H_{15}O_{12}$ ($M_r = 472.5$) (%), C, 22.88, H, 3.20, found: C, 22.88, H, 2.88. FTIR (cm^{-1}): ν(O–H) = 3478 (s), 3403 (s), 3336 (s), 3253 (s), $\nu(\mathrm{C–H})_{arom}$ = 3092 (m), ν(C–O) and $\nu(\mathrm{C–C})_{arom}$ = 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 $K_{\alpha1,2}$ radiation.

Theoretical methods. The DFT calculations were performed using the ORCA 3.0.3 computational package.[42] The relativistic effects were included in all the calculations using the scalar relativistic contracted version of the def2-TZVPP basis functions[43] and with the zero-order regular approximation (ZORA).[44] The single point energy calculations were based on the molecular geometry derived from experimental X-ray data (Cambridge Structural Database (CSD),[45] code RAVJUV) utilizing the B3LYP functional.[46–48] The isotropic exchange constant J were calculated by comparing the energies of high-spin (HS) and broken-symmetry (BS) spin states utilizing both Ruiz's approach[49] and Yamaguchi's approach.[50] The figure showing structural motif was done with Diamond software[51] and spin density plot with VESTA 3 software.[52]

Acknowledgements

We acknowledge the financial support from the National Programme of Sustainability I (LO1305) 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 Šafárik 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. Nanobiotechnol.*, 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. Roubeau 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. Roubeau, 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. Prokleška, V. Sechovský 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, **98**, 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.