

Observation of a large magnetocaloric effect in a
2D Gd(III)-based coordination polymer†Cite this: *Dalton Trans.*, 2013, **42**, 13331

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A new 2D Gd(III)-based coordination polymer has close to the highest cryogenic magnetocaloric effect of any MOF reported so far. The experimental results reveal its structural features and magnetic properties.

Experimental observations indicate that the magnetocaloric effect (MCE) of molecule-based materials can efficiently outperform and economically replace conventional compressor-based refrigeration at ultra-low temperature.^{1,2} The magnetocaloric effect can be described as the change of the magnetic entropy and adiabatic temperature in response to a change in the applied magnetic field, and can be exploited for magnetic refrigeration in a process known as adiabatic demagnetization. The magnitude of the MCE of a magnetic material is characterized by ΔS_m , the isothermal magnetic entropy change, and ΔT_{ad} , the adiabatic temperature change.

The total entropy of a magnetic material in which the magnetism is due to localized moments, such as lanthanide based materials, can be expressed as $S(T)P = [S_l(T) + S_e(T) + S_m(T)]P$, where S_l , S_e and S_m are the lattice, electronic and magnetic entropy, respectively.^{3–5} Apparently, among these three contributions, only the magnetic entropy is strongly field-dependent. Consequently, for an isobaric–isothermal process, the differential for the total entropy can be represented as $\Delta S_m(T, \Delta H)$. However, the correct theoretical description of the MCE is complicated and far from being comprehensive.⁶ The magnitude of the magnetic refrigeration is proportional to the size of the magnetic moments and to the applied magnetic field. The magnetic field can easily be applied using commercially available permanent magnets. Our effort in looking for advanced synthetic materials as efficient magnetic refrigerants in modest magnetic fields resulted in a new layered metal–organic framework (MOF), $[\text{Gd}(\text{C}_4\text{O}_4)(\text{OH})(\text{H}_2\text{O})_4]_n$ (**1**). We

chose Gd^{3+} as a constituent element, as a large MCE can be achieved for reasons such as: (a) its large spin ground state, which provides the largest entropy per single ion, and amounts to $R \ln(2S + 1)$, (b) its zero orbital momentum, which implies that the crystal field effects are extremely small, and (c) its weak superexchange interactions, which result in low-lying excited spin states.

Our choice of ligand was inspired by the recent report of conductivity shown by squaric acid in a crystal lattice and based on the intent of preparing a higher dimensional molecule.⁷ The small size of the squaric acid was expected to provide a high density of metals, and the exchange pathways through the ligand were likely to result in weak superexchange interactions between the metal centres. The majority of the MCE studies were carried out on the high spin 0D Gd-cluster⁸ with the aim of achieving a high density of metal ions assembled by a minimum number of ligands.

Compound **1** was crystallized in the monoclinic $P2_1/c$ space group, and the asymmetric unit contains one six-coordinated Gd^{3+} ion (Fig. S1†).⁹ The metal centres are coordinated by three oxo groups from the squarate ligand, four water ligands, and one hydroxyl oxygen. The Gd^{3+} ions form a chain propagating along the b -axis through a single squarate anti–anti bridge (Fig. 1, 2 and S2†). The squarate ligands of the adjacent chains

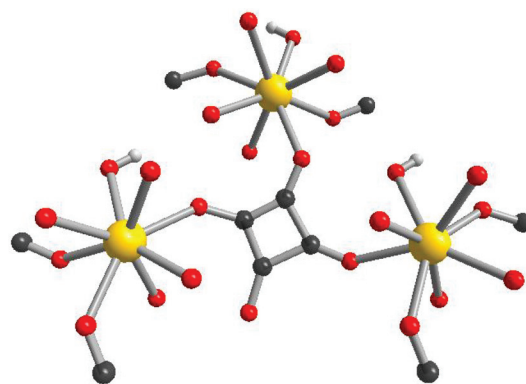


Fig. 1 In-layer bridging mode of squarate and the coordination environment of Gd^{3+} . Colour code: Gd yellow, C gray, O red.

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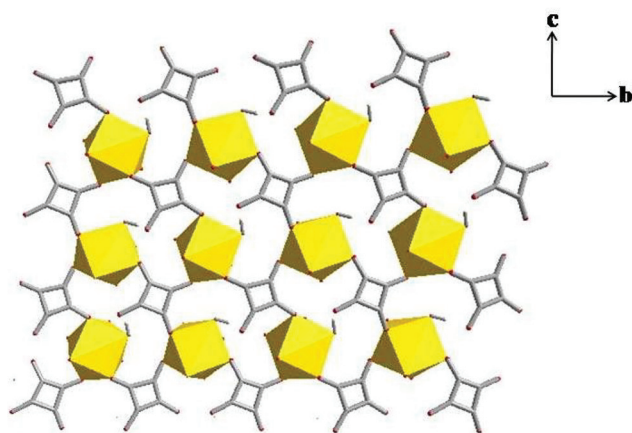


Fig. 2 Polyhedral view of **1** along the *a*-axis.

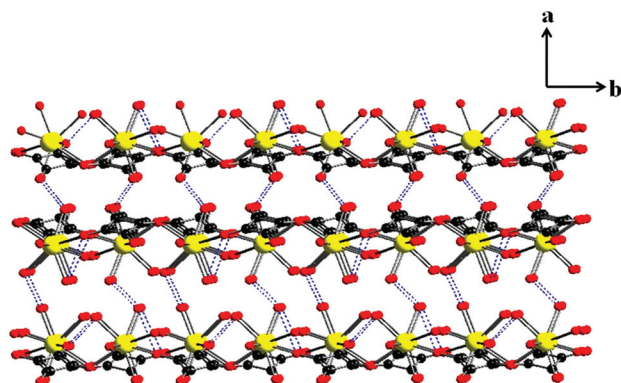


Fig. 3 Packing diagram of **1** along the *c*-axis. H-bonding connectivities between adjacent planes. Colour code: Gd yellow, C gray, O red.

are rotated by $\sim 90^\circ$ and alternatively connected to the Gd^{3+} ions of the adjoining chains in both sides *via* their third oxo group along an axis to form a 2D sheet structure (Fig. 2). Interestingly, the squarate ligands are situated above the metal pseudo plane and tilted at an angle of 77° (Fig. S3†).

The average in-layer Gd–Gd separation is $6.48(1)$ Å. Extensive intra- and interlayer hydrogen bonding between squarate oxygens and the water ligands (Table S1†) generate an extended structure along the *c*-axis (Fig. 3). The true topology of **1** is therefore better described as 3D.

A list of selected molecular compounds based on gadolinium and their magnetic entropy changes are given in Table 1. To date, the number of reported molecular magnetic refrigerants with higher dimensionality is very limited.¹⁰ The title compound was prepared in good yield by a slow diffusion method at room temperature. A thermogravimetric analysis (Fig. S4†) of **1** shows that coordinated H_2O molecules are eliminated from the network at $\sim 130^\circ\text{C}$; decomposition of the framework occurs at $\sim 450^\circ\text{C}$ which indicates the robustness of the framework. The bulk phase powder X-ray diffraction

Table 1 Temperature (T_m) and values of the maximum of magnetic entropy change (ΔS_m^{max}) for selected compounds based on gadolinium

Material	T_m	$-\Delta S_m^{\text{max}}$	Ref.
$\text{Gd}_7(\text{OH})_6$ ^c	3	23 ^a	3b
$\text{Gd}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$	1.2	40 ^a	4a
$\text{Gd}(\text{HCOO})(\text{bdc})$	2.2	47 ^b	3c
$\text{Gd}(\text{HCOO})(\text{OAc})_2(\text{H}_2\text{O})_2$	1.8	45.9 ^a	3d
$[\text{Gd}(\text{C}_4\text{O}_4)(\text{OH})(\text{H}_2\text{O})_4]_n$	<3.0	43.8 ^a , 47.3 ^b	This work
$[\text{Gd}(\text{OAc})_3(\text{H}_2\text{O})_{0.5}]_n$	1.8	47.7	4n

^a $\mu_0\Delta H = 7$ T. ^b $\mu_0\Delta H = 9$ T. ^c Metal nuclearity; see reference for complete formula.

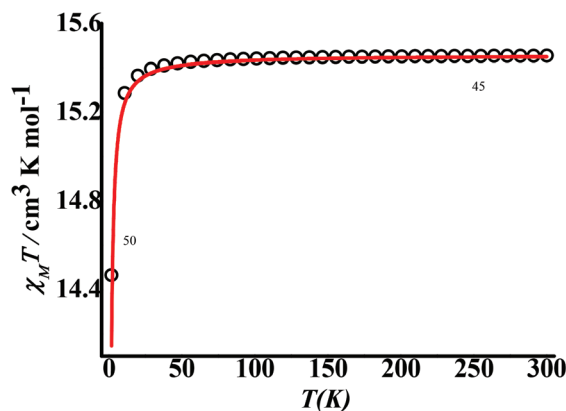


Fig. 4 Temperature dependence of the dc susceptibility in the form of $\chi_M T$ collected in an applied field of 0.1 T. The solid line represents the best fit obtained.

pattern of the polycrystalline sample is in good agreement with the simulated one based on the single crystal structure data (shown in Fig. S5†), indicating that the as-synthesized product is pure. The powder samples were used for magnetic property measurements.

The magnetic behaviour of the compound is shown in the form of $\chi_M T$ (χ_M = molar magnetic susceptibility) *vs.* *T* plot in Fig. 4.

The room-temperature experimental value of $\chi_M T$ agrees with that expected ($15.6 \text{ cm}^3 \text{ K mol}^{-1}$, for $g = 2.0$) for two non-interacting Gd^{3+} ions with $g = 2$, that is $\chi_M T = 15.45 \text{ cm}^3 \text{ K mol}^{-1}$. On lowering *T*, $\chi_M T$ stays nearly constant with decreasing temperature down to approximately 40 K, below which it decreases significantly, reaches a value of $14.46 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K, thus corroborating the dominant antiferromagnetic coupling between the Gd^{3+} ions.

The magnetic data were simulated following the Curie equation which gave the best fitting values of $C = 15.46 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and $\theta = -0.12(4) \text{ K}$. A very low negative θ value indicates that the interactions between adjacent Gd^{3+} centers are weak and antiferromagnetic in nature or can also be attributed to the saturation effect. Magnetization measurements between 2 and 10 K (Fig. 5) show a steady increase with increasing magnetic field (*H*) and become saturated at 9 T. The plot $M/N\mu_B$ *vs.* H/T (Fig. S6†) also shows that all magnetisation isotherms

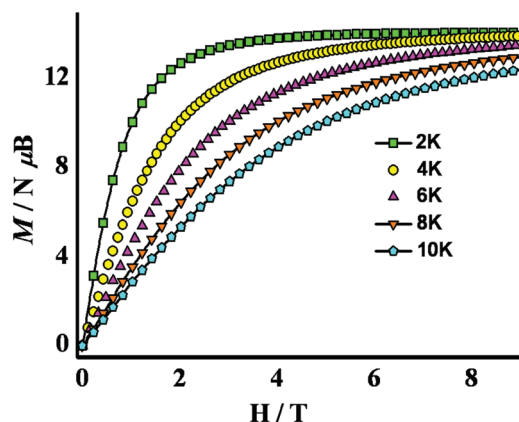


Fig. 5 Field-dependencies of isothermal normalized magnetizations for two Gd^{3+} ions, collected for temperatures ranging from 2 to 10 K.

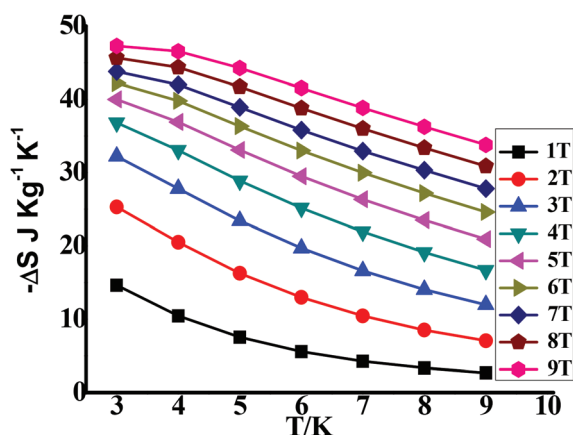


Fig. 6 Temperature dependencies (3 K to 10 K) of the magnetic entropy change ($-\Delta S_m$) as obtained from the magnetization data.

collapse on the same master curve, indicating that Gd^{3+} is very isotropic (no zfs effects) as expected.

The magnetic entropy changes, ΔS_m , are calculated from the magnetization data by means of the Maxwell relation: $\Delta S_m(T, \Delta H) = \int [\partial M(T, H)/\partial T]_H dH$.¹¹ The results are shown in Fig. 6 as a function of T and for several field changes $\Delta H_0 = H_f - H_i$, where f and i indicate the final and initial states, respectively. The maximum entropy change is obtained as $-\Delta S_m = 47.3 \text{ J kg}^{-1} \text{ K}^{-1}$ for a field change of $\Delta H_0 = 9 \text{ T}$. The entropy change is close to the highest value reported ($-\Delta S_m \sim 56 \text{ J kg}^{-1} \text{ K}^{-1}$)⁴⁰ so far for any MOF system.

Conclusion

In summary, we report a large cryogenic MCE observed for Gd-based magnetic refrigerant materials of higher dimensionality. At liquid helium temperatures and for typically applied fields, the MCE is largely determined by the Gd density in the

material. It can be easily imagined that the major research interest on magnetic refrigerant materials may now move towards molecules based on lightweight bridging ligands such as squarate, so that the ideal limit of an infinite ratio of non-interacting Gd^{3+} ions can be achieved. It is also evident that the remarkable flexibility of synthetic chemistry can lead the search for new magnetic refrigerant materials which may not be restricted by the limitation of planned synthesis.

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Notes and references

- (a) Y. C. Zimm, A. Jastrab, A. Sternberg, V. Pecharsky, A. Gschneidner Jr., M. Osborne and I. Anderson, *Adv. Cryog. Eng.*, 1998, **43**, 1759; (b) V. Pecharsky and A. Gschneidner Jr., *J. Magn. Magn. Mater.*, 1999, **200**, 44.
- (a) F. B. Yu, Q. Gao, B. Zhang, Z. X. Meng and Z. Chen, *Int. J. Refrig.*, 2003, **26**, 622; (b) V. Pecharsky and A. Gschneidner Jr., *Int. J. Refrig.*, 2006, **29**, 1239; (c) A. Gschneidner Jr. and V. Pecharsky, *Int. J. Refrig.*, 2008, **31**, 945.
- (a) E. Warburg, *Ann. Phys. Chem.*, 1881, **13**, 141; (b) J. W. Sharples, Y. Z. Zheng, F. Tuna, E. J. L. McInnes and D. Collison, *Chem. Commun.*, 2011, **47**, 7650; (c) R. Sibille, T. Mazet, B. Malaman and M. François, *Chem.-Eur. J.*, 2012, **18**, 12970; (d) G. Lorusso, M. A. Palacios, G. S. Nichol, E. K. Brechin, O. Roubeau and M. Evangelisti, *Chem. Commun.*, 2012, **48**, 7592; (e) M. M. Canovas, C. E. T. Eeckalaers, L. Catala, W. Wernsdorfer, E. K. Brechin and T. Mallah, *Inorg. Chem.*, 2006, **45**, 7038; (f) M. I. Khan and J. Zubieta, *Prog. Inorg. Chem.*, 1995, **43**, 1; (g) T. C. Stamatatos, A. K. Abboud, W. Wernsdorfer and G. Christou, *Angew. Chem.*, 2006, **118**, 4240; (h) S. Wang, H. L. Tsai, E. Libby, K. Folting, W. E. Streib, D. N. Hendrickson and G. Christou, *Inorg. Chem.*, 1996, **35**, 7578; (i) G. Aromi, M. J. Knapp, J. P. Claude, J. C. Huffman, D. N. Hendrickson and G. Christou, *J. Am. Chem. Soc.*, 1999, **121**, 5489; (j) D. P. Goldberg, A. Caneschi, C. D. Delfs, R. Sessoli and S. J. Lippard, *J. Am. Chem. Soc.*, 1995, **117**, 5789.
- (a) M. Evangelisti, O. Roubeau, E. Palacios, A. Camon, T. N. Hooper, E. K. Brechin and J. J. Alonso, *Angew. Chem., Int. Ed.*, 2011, **50**, 6606; (b) Y. Z. Zheng, M. Evangelisti and R. E. P. Winpenney, *Chem. Sci.*, 2011, **2**, 99; (c) Y. Z. Zheng, M. Evangelisti and R. E. P. Winpenney, *Angew. Chem., Int. Ed.*, 2011, **50**, 3692; (d) Y. Z. Zheng, E. M. Pineda,

- M. Helliwell and R. E. P. Winpenny, *Chem.-Eur. J.*, 2012, **18**, 4161; (e) M. Manoli, R. D. L. Johnstone, S. Parsons, M. Murrie, M. Affronte, M. Evangelisti and E. K. Brechin, *Angew. Chem., Int. Ed.*, 2007, **46**, 4456; (f) T. N. Hooper, J. Schnack, S. Piligkos, M. Evangelisti and E. K. Brechin, *Angew. Chem., Int. Ed.*, 2012, **51**, 4633; (g) G. Karotsis, M. Evangelisti, S. J. Dalgarno and E. K. Brechin, *Angew. Chem.*, 2009, **121**, 10112, (*Angew. Chem., Int. Ed.*, 2009, **48**, 9928); (h) V. Mereacre, M. N. Akhtar, Y. Lan, A. M. Ako, R. Clerac, C. E. Anson and A. K. Powell, *Dalton Trans.*, 2010, **39**, 4918; (i) R. Sessoli, *Angew. Chem., Int. Ed.*, 2012, **51**, 43; (j) S. Goswami, A. Adhikary, H. S. Jena and S. Konar, *Dalton Trans.*, 2013, DOI: 10.1039/C3DT51974K; (k) F. S. Guo, Y. C. Chen, J. L. Liu, J. D. Leng, Z. S. Meng, P. Vrabel, M. Orendac and M. L. Tong, *Chem. Commun.*, 2012, **48**, 12219; (l) E. Colacio, J. Ruiz, G. Lorusso, E. K. Brechin and M. Evangelisti, *Chem. Commun.*, 2013, **49**, 3845; (m) M. Wu, F. Jiang, X. Kong, D. Yuan, L. Long, S. A. L. Thabaiti and M. Hong, *Chem. Sci.*, 2013, **4**, 3104; (n) F. S. Guo, J. D. Leng, J. L. Liu, Z. S. Meng and M. L. Tong, *Inorg. Chem.*, 2012, **51**, 405; (o) 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, DOI: 10.1002/adma.201301997.
- 5 (a) J. Liu, T. Gottschall, K. P. Skokov, J. D. Moore and O. Gutfleisch, *Nat. Mater.*, 2012, **11**, 620; (b) S. C. Riggs, O. Vafek, J. B. Kemper, J. B. Betts, A. Migliori, F. F. Balakirev, W. N. Hardy, R. Liang, D. A. Bonn and G. S. Boebinger, *Nat. Phys.*, 2011, **7**, 332; (c) C. Benelli and D. Gatteschi, *Chem. Rev.*, 2002, **102**, 2369.
- 6 P. Kumar, K. N. Singh, K. G. Suresh, A. K. Nigam and S. K. Malik, *J. Appl. Phys.*, 2005, **97**, 10A301-1.
- 7 S. Horiuchi, Y. Tokunaga, G. Giovannetti, S. Picozzi, H. Itoh, R. Shimano, R. Kumai and Y. Tokura, *Nature*, 2010, **463**, 789.
- 8 (a) O. Tegus, E. Bruck, K. H. J. Buschow and F. R. de Boer, *Nature*, 2002, **415**, 150; (b) V. K. Pecharsky and K. A. Gschneidner Jr., *Adv. Mater.*, 2001, **13**, 683.
- 9 Crystal data: $\text{C}_4\text{GdO}_9\text{H}_9$, monoclinic, $P2_1/c$, $a = 11.8981(6)$, $b = 8.1956(5)$, $c = 10.0764(5)$ Å, $\beta = 96.396(3)^\circ$, $V = 976.46(9)$ Å³, $M = 350.30$, $D_c = 2.383$ g cm⁻³, $Z = 4$, $R_1 = 0.0257$ for 1986 reflections. CCDC no. 900722 for **1** contains the supplementary crystallographic data for this paper.
- 10 (a) M. J. M. Pérez, O. Montero, M. Evangelisti, F. Luis, J. Sesé, S. C. Serra and E. Coronado, *Adv. Mater.*, 2012, **24**, 4301; (b) Y. Li, F.-K. Zheng, X. Liu, W.-Q. Zou, G.-C. Guo, C.-Z. Lu and J.-S. Huang, *Inorg. Chem.*, 2006, **45**, 6308.
- 11 M. H. Phan and S. C. Yu, *J. Magn. Magn. Mater.*, 2007, **308**, 325.