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Field-induced slow magnetic relaxation and magnetocaloric effects in an oxalato-bridged gadolinium(III)-based 2D MOF⁺

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The coexistence of field-induced slow magnetic relaxation and moderately large magnetocaloric efficiency in the supra-Kelvin temperature region occurs in the 2D compound $[Gd_2^{III} (ox)_3(H_2O)_6]_n \cdot 4nH_2O$ (1), a feature that can be exploited in the proof-of-concept design of a new class of slow-relaxing magnetic materials for cryogenic magnetic refrigeration.

Lanthanide(III) metal-organic frameworks (MOFs) have attracted much attention in the last decade because of their potential technological applications in Quantum Information Processing (QIP) and Cryogenic Magnetic Refrigeration (CMR).¹⁻⁶ The high spin ground state and almost-negligible magnetic anisotropy of Gd^{III} ions, combined with an extremely low magnetic ordering temperature due to the weak exchange magnetic interactions, make gadolinium(m)-based MOFs of varying dimensionalities very good candidates as magnetic molecular coolers for CMR.⁷⁻¹⁶ Among them, a rare class of Gd^{III} MOFs with field-induced slow magnetic relaxation (SMR), typical of mononuclear gadolinium(III) single-ion magnets (SIMs),^{17,18} referred to as Gd^{III} SIM-MOFs, are ideally suited for CMR investigations due to their well-known magnetocaloric (MCE) and spin-lattice relaxation (SLR) effects.^{19,20} Hence, large changes in the isothermal magnetic entropy (ΔS_m) and adiabatic temperature (ΔT_{ad}) are expected to occur when switching off the applied magnetic field in the neighborhood of the magnetization blocking temperature. In terms of not only chemical stability and tunability but also addressing scalability, Gd^{III} SIM-MOFs are superior to their Gd^{III} SIMs analogues, which have been recently investigated both as proto-

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types of quantum bits (qubits) for QIP and ultra-low temperature (sub-Kelvin) molecular coolers for CMR.²¹

We are particularly interested in the well-known family of 2D and 3D Ln MOFs prepared by using the simplest dicarboxylic acid, oxalic acid, as a lightweight organic bridging ligand for the design and synthesis of cryogenic magnetic coolers (Table S1, ESI†). Herein, we report our first results along this line concerning the synthesis, structural characterization, and magnetic and magnetothermal properties of a gadolinium(III) sesquioxalate decahydrate of formula $[Gd_2^{III}$ $(ox)_3(H_2O)_6]_n \cdot 4nH_2O$ (1). Compound 1 is a rare example of 2D Gd^{III} SIM-MOFs displaying SMR and MCE at the same time, being proposed as a new class of low-temperature (supra-Kelvin) slow-relaxing magnetic refrigerant material.

Colorless plates of **1** suitable for single-crystal X-ray diffraction (XRD) have been obtained in a pure form and good yield (*ca.* 70%) by slow diffusion of aqueous solutions of oxalic acid (H₂ox) and GdCl₃·6H₂O (3 : 2 molar ratio) into an H-shaped tube after several weeks at 50 °C (see the Experimental section and Table S2, ESI†). The crystal structure of **1** is made up of neutral oxalato-bridged gadolinium(III) layers of honeycomb type with a hexagonal net topology (6³-hcb), together with both coordinated and disordered hydrogen-bonded crystallization water (Fig. 1 and Fig. S1–S3, ESI†), as reported earlier for [Gd^{III}₂ (ox)₃(H₂O)₆]_n·2.5*n*H₂O (**1**').²²

The crystallographically independent gadolinium atom of **1** has a nine-coordinate environment formed by six oxygen atoms from three bis-bidentate oxalato bridging ligands (μ -oxalato- $\kappa^2 O$,O': $\kappa^2 O'$,O''') plus three oxygen atoms from the three coordinated water molecules (Fig. S1†). The spherical-type distorted metal coordination polyhedron is an intermediate between a tricapped trigonal prism (TCTPR) and a mono-capped square antiprism (CSAPR), as supported by the continuous shape measures (CShM = 0.714 and 0.790, respectively).²³ Interestingly, the asymmetric propeller-like tris (chelate) mononuclear units are chiral, as reported earlier for **1**',²² so that the two helical enantiomers, (*M*)- and (*P*)-



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Fig. 1 Projection views of the neutral oxalato-bridged gadolinium(III) hexagonal layer and the crystal packing of adjacent layers of 1 along the crystallographic b (top) and a axes (bottom). The two centrosymmetrically related mononuclear units of opposite chiralities are shown as dark and light purple spheres (top), while the adjacent layers are shown in different colors for clarity (bottom). Hydrogen bonds between the coordinated water molecules and the oxalato bridges are shown as dashed lines.

 $[Gd^{III}(ox)_{3/2}(H_2O)_3]$, are present in their crystal structures giving rise to achiral μ -oxalato- $\kappa^2 O$, $O':\kappa O''$, O'''-gadolinium(III) layers growing in the *ac* plane (Fig. 1, top).

In the crystal lattice of **1**, the adjacent oxalato-bridged gadolinium(m) hexagonal layers are stacked along the crystallographic *b* axis (Fig. 1, bottom). However, they are not eclipsed but displaced by half a unit cell along the crystallographic *c* axis giving rise to an *-ABA-* sequence (Fig. S3,† left). Overall, this interlayer packing leads to small hexagonal pores along the [011] direction, in which the hydrogen-bonded, coordinated and free water molecules are placed (Fig. S3,† right).

The intralayer voids within the hexagonal rings are occupied by free water molecules that are hydrogen-bonded to each other $[Ow\cdots Ow = 2.85 \text{ Å}]$ or to the oxalato bridging groups $[Ow\cdots O = 3.01 \text{ Å}]$ (Fig. S2,† top). The interlayer space is occupied by additional free water molecules that establish moderate hydrogen bonds with the oxalato bridges (Ow···O = 2.75–2.76 Å) and with both the intralayer crystallized (Ow···Ow = 2.67–2.80 Å) and coordinated water molecules (Ow···Ow = 2.68–2.85 Å) (Fig. S2,† bottom). In addition, moderate to weak hydrogen bonds are formed among the coordinated water molecules and the oxalato bridging groups from adjacent layers [Ow···O = 2.68–3.03 Å], thereby leading to a dense packed, hydrogen-bonded multilayer structure (Fig. 1, bottom). Hence, the shortest interlayer metal separation through the hydrogen-bonded coordinated water molecules (Gd···Gd =

6.127 Å) is even shorter than the intralayer metal distances across the oxalato bridges (Gd \cdots Gd = 6.306–6.457 Å).

The static magnetic properties of 1 were measured on frozen matrix water suspensions to prevent partial water loss (see the Experimental section). The $\chi_{M}T vs. T$ plot shows very small deviations from the Curie law behaviour in the temperature range 2.0–300 K (Fig. S4, ESI[†]). The small decay of $\chi_{\rm M}T$ at low temperatures is likely due to the very weak intralayer antiferromagnetic interactions between the Gd^{III} ions across the oxalato bridge, as reported earlier for 1'.²² The least-squares fit of the magnetic susceptibility data of 1 through an empirical law ($\gamma IS(S + 1)$ vs. T/IS(S + 1) with S = 7/2) obtained from a Monte Carlo simulation on a 2D honeycomb network using a classical spin approach gave g = 2.0040(7) and J = -0.0205(5)cm⁻¹, where g is the isotropic Landé factor of the Gd^{III} ion and *J* is the magnetic coupling parameter (Fig. S4,† inset).²⁴ The calculated -/ value for 1 is very small but non-negligible, being four-fold higher than that previously reported for 1' [-J = 0.0050(2) K].²² This scenario agrees with the isothermal magnetisation at 2 K that slightly deviates from the Brillouin function for the sum of two isolated octets (S = 7/2) reflecting a very weak intralayer antiferromagnetic interaction between the Gd^{III} ions (Fig. S5, ESI[†]). The *M* vs. *H*/*T* plots in the temperature range of T = 2.0-20 K show superimposable curves, indicating a negligible anisotropy of the Gd^{III} ions (Fig. S5,† inset).

When measuring the dynamic magnetic properties of 1 at a fixed frequency of $\nu = 1000$ Hz under different applied dc magnetic fields (H = 0, 0.1 and 0.25 T), a field-induced SMR behaviour was observed (Fig. S6, ESI†). When no bias field is applied, neither $\chi'_{\rm M}$ maximum nor $\chi''_{\rm M}$ signal were observed. However, when a relatively small dc magnetic field is applied (H = 0.1 T), a shoulder appears in the high-temperature tail of the $\chi'_{\rm M}$ vs. *T* plot (Fig. S6,† left), while the $\chi''_{\rm M}$ vs. *T* plot shows a distinct maximum at $T_{\rm max} = 5.0$ K for $\nu = 1000$ Hz (Fig. S6,† right). Moreover, upon increasing the magnitude of the dc magnetic field (H = 0.25 T), a distinct $\chi'_{\rm M}$ maximum is observed (Fig. S6,† left), while the $\chi''_{\rm M}$ maximum is normal shifts towards higher temperatures, up to $T_{\rm max} = 8.0$ K for $\nu = 1000$ Hz (Fig. S6,† right).

A magnetic field of H = 0.25 T was then selected to scan the $\chi'_{\rm M}$ and $\chi''_{\rm M}$ vs. temperature response for 1 in the frequency range of $\nu = 40-10\,000$ Hz (Fig. 2). Under these conditions, a single maximum appears in the $\chi''_{\rm M}$ vs. *T* plot, whose intensity decreases continuously upon increasing the frequency of the oscillating ac field of ±5 Oe and progressively shifts toward higher blocking temperatures, from $T_{\rm max} = 4.0$ up to 12.0 K (Fig. 2, bottom).

The values of the magnetic relaxation time (τ) for **1** at H = 0.25 T can be calculated from the joint analysis of the $\chi'_{\rm M}$ and $\chi''_{\rm M} vs.$ frequency plots through the generalised Debye model (Fig. S7, ESI†), which considers the adiabatic ($\chi_{\rm S}$) and isothermal ($\chi_{\rm T}$) magnetic susceptibilities, as well as the exponential factor (α), as additional fitting parameters. The corresponding Argand plots at H = 0.25 T in the temperature range 2.5–11.0 K can be perfectly simulated with the calculated values of α , $\chi_{\rm S}$ and $\chi_{\rm T}$ parameters obtained from the general-



Fig. 2 Temperature dependence of χ'_{M} (top) and χ''_{M} (bottom) for **1** at an oscillating magnetic field of ± 5 Oe in the frequency range $\nu = 40-10\,000$ Hz (blue to red) and H = 0.25 T. The solid lines are only eyeguides. The inset shows the Arrhenius plot in the temperature range 2.5–11 K. The solid line is the best-fit curve (see text).

ised Debye model fitting (Fig. S8, ESI†). This fact suggests a single relaxation path in contrast to the double magnetic relaxation process earlier reported for the related dysprosium(m) oxalate decahydrate analogue of formula $[Dy_2^{II}(ox)_3(H_2O)_6]_n$. $4nH_2O$.²⁵ The calculated relatively low values of the α parameter ($\alpha = 0.075-0.195$) support a narrow distribution of τ in the single magnetic relaxation process.

The calculated τ values for **1** at H = 0.25 T are represented in the form of the $\ln(\tau)$ *vs.* 1/T (so-called Arrhenius) plot (in agreement with was done the ordinate scale in the inset of Fig. 2 bottom). The experimental data deviate from the linear Arrhenius law characteristic of a single thermally activated magnetic relaxation process. Instead, they begin to saturate at low temperatures indicating the presence of a temperatureindependent magnetic relaxation. The fitting of the Arrhenius plot between 2.5 and 11.0 K is in good agreement with the following equation:

$$\tau^{-1} = \tau_{\rm IK}^{-1} + CT^n, \tag{1}$$

where the two terms correspond to intraKramers (IK) and Raman relaxation mechanisms, respectively, yielding the best fitting values of $\tau_{IK} = 0.0162(6)$ s, C = 0.028(3) s⁻¹ K⁻ⁿ and n = 5.83(4).

The IK contribution in the low-temperature region (T < 3 K) should be seen as a zero-order term associated with a slower passage between the two components $m_{\rm S} = \pm 1/2$ (S = 7/2), where the conversion is feasible, and not as a quantum tunneling of the magnetisation (QTM) of the Zeeman-splitted $m_{\rm S}$ levels, which is inconsistent with an isotropic Gd^{III} ion. Remarkably, the calculated τ_{IK} value for 1 at H = 0.25 T is rather high, being comparable with those earlier reported for the QTM regime in mononuclear gadolinium(m)-based polyoxometalates (POMs) which exhibit SMR effects at very low temperatures ($T_{\rm B}$ < 0.1 K) in the absence of an applied magnetic field ($\tau_{\text{OTM}} = 0.000015 - 0.05 \text{ s}$).¹⁷ On the other hand, the calculated *n* value for **1** at H = 0.25 T is slightly lower than that expected for a Kramer ion (accepted n = 6-8). However, it is higher than those previously reported for the related example of 3D Gd^{III} SIM-MOFs, namely the gadolinium(III) fumarate heptahydrate of formula $[Gd_2^{III}(fum)_3(H_2O)_4]_n \cdot 3nH_2O$ (Gd-fum), which has been recently proposed as a cryogenic magnetic cooler.¹⁹ In this case, the authors argued that the SMR effects are not associated with a magnetic anisotropy energy barrier but with a resonant phonon trapping through a phonon-bottleneck process (n = 2.6 at H = 0.1 T).²⁰ The two different processes in the relaxation are represented in the different slopes of a log-log plot (Fig. S10[†]).

The magnetothermal properties of **1** have been investigated by variable-temperature (T = 2.0-20 K, with $\Delta T = 1$ K) and variable-field (H = 0-8 T, with $\Delta H = 0.2$ T) magnetisation measurements (see the Experimental section, Fig. S9, ESI†). The magnetic entropy change ($\Delta S_{\rm M}$) for a selected magnetic field change ($\Delta H = H - H_0$ with $H_0 = 0$) can then be estimated from the *M* vs. *T* and *H* plots using the Maxwell equation.²⁶

The $-\Delta S_{\rm M}$ vs. T and H plots for 1 increase monotonically upon increasing the magnetic field variation or decreasing the temperature, respectively (Fig. 3). No maximum of $-\Delta S_{\rm M}$ was observed at T > 2 K for $\Delta H < 8$ T. In contrast, the related 2D gadolinium(III) sesquioxalate hydrate of formula $[Gd_2^{III}(ox)_3(H_2O)_6]_n \cdot 0.6nH_2O(1'')$ shows a $-\Delta S_M$ maximum for 1 around 2.75 K for magnetic field changes higher than 7.0 T, even if it remains paramagnetic with no field-induced SMR behaviour above 2 K.¹⁴ The lack of $-\Delta S_{M}$ maxima for **1** suggests that the SMR effects do not enable the observation of a large MCE in the pure IK quantum regime of this Gd^{III} SIM-MOF (T < 3 K). In fact, the $-\Delta S_{\rm M}$ values (in molar units) of 31.5 (1) and 33.1 J mol⁻¹ K⁻¹ (1") at T = 2 K and $\Delta H = 8$ T are similar, being close to the limiting value for two magnetically isolated, isotropic Gd^{III} ions $[\Delta S_{\rm M} = 2R \ln(2S + 1) = 4.16R = 34.6 \text{ J mol}^{-1} \text{ K}^{-1}$ with S = 7/2].

The MCE efficiency of **1** is among the largest ones yet reported for the related Gd^{III} MOFs proposed as cryogenic magnetic coolers (Table S3, ESI†). Hence, the $-\Delta S_M$ value (in gravimetric units) of 41.5 J kg⁻¹ K⁻¹ for **1** at T = 2 K and $\Delta H = 8$ T compares well with those of the more dense 3D Gd^{III} MOFs



Fig. 3 Temperature dependence of $-\Delta S_M$ for **1** in the magnetic field range 0–8 T (blue to red) (top). Field dependence of $-\Delta S_M$ in the temperature range 2–20 K (blue to red)(bottom). The solid lines are only eyeguides.

reported in the literature $(-\Delta S_{\rm M} = 40.6-60.0 \text{ J kg}^{-1} \text{ K}^{-1} \text{ at } T = 2 \text{ K and } \Delta H = 7 \text{ T}$; Table S3,† entries 2, 4–8, 12, and 13).^{7–12} This situation conforms with the presence of the lightweight oxalate ligand, which leads to a relatively high percentage mass ratio of magnetic/non-magnetic atoms.^{13–16} Moreover, the $-\Delta S_{\rm M}$ value of 21.9 J kg⁻¹ K⁻¹ for 1 at T = 2 K and $\Delta H = 2 \text{ T}$ are somewhat higher than that of the aforementioned Gd^{III} SIM-MOF with the heavier fumarate bridging ligand $(-\Delta S_{\rm M} = 18.0 \text{ J kg}^{-1} \text{ K}^{-1}$ at T = 1 K and $\Delta H = 2 \text{ T}$.¹⁹ This low magnetic field is sufficiently close to the stronger one that can be achieved with the common permanent magnets used commercially (ranging from 0.5 to 1 T for ceramic magnets and up to 1.4 T for the neodymium ones). This feature is mandatory for the practical applications of 2D gadolinium(III) sesquioxalates as cryogenic magnetic coolers.

In summary, compound **1** constitutes a unique example of Gd^{III} SIM-MOF displaying SMR effects at moderately high blocking temperatures in the presence of a relatively low applied magnetic field. Interestingly, it exhibits moderate to large MCE for relatively low variations in the applied magnetic

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field. Both features allow this novel class of field-induced Gd^{III} SIM-MOFs with a dense-packed oxalato-bridged gadolinium(III) hexagonal layer structure to be proposed as candidates as low-temperature molecular magnetic refrigerant materials for CMR. Current efforts are devoted to preparing magnetically diluted samples in order to further investigate the SMR behaviour, as well as the quantum coherence properties in this ordered 2D array of potential qubits for QIP.

Conflicts of interest

There are no conflicts to declare.

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