Exploring the magnetocaloric effect in the *Ln*$(HCO_2)(C_2O_4)$ family of Metal-Organic Frameworks

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Low-temperature cooling is a necessary requirement in many areas of fundamental research and applied technologies. Many applications, including quantum computing[1], spintronics[2] and medical imaging, rely on liquid helium to operate at temperatures below 20 K. In particular, liquid helium ^{4}He is used for T > 2 K and a mixture of the two isotopes ^{3}He and ^{4}He is commonly employed for cooling below this. Liquid helium is costly, expensive and prone to disruptions in supply,[3] so it is necessary to explore efficient and cost-effective alternatives. Paramagnetic magnetocalorics[4] are great He-free candidates for low-temperature cooling, with much higher thermodynamic efficiencies below 20 K than cryocoolers, although most magnetocalorics are tailored for use below 1 K and very high applied fields.

Recent work on coordination frameworks have shown compound such as $Gd(HCO_2)_3$ and $GdOHCO_3$, having comparable or greater MCEs than $Gd_3Ga_5O_{12}$ (GGG), the benchmark magnetocaloric for cooling below 10 K, with the incorporation of other lanthanides leading to excellent performance above 4 K in low applied fields.[5,6,7] Inspired by these results we have synthesised members of the *Ln*$(HCO_2)(C_2O_4)$ family (*Ln* = Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}) that crystallise in the orthorhombic P*nma* space group and feature low-dimensional chains arranged on a distorted triangular lattice. We have studied the magnetic properties and MCE of these materials.

We have found $Gd(HCO_2)(C_2O_4)$ to be an excellent candidate for applications at around 2 K with one of the highest magnetocaloric entropy changes amongst coordination frameworks. Generally, the incorporation of Ising-like cations was previously shown to lead to improved performance at higher temperatures under low applied fields that can be generated more easily using permanent magnets. We have observed this only for $Dy(HCO_2)(C_2O_4)$, in contrast with results found for the *Ln*$(HCO_2)_3$ and *Ln*$OHCO_3$ families of compounds. Indeed, characterisation using neutron diffraction indicates these Ising compounds lack the strong local magnetic correlations found in the related analogues, indicating this negatively affects the optimisation of the MCE performance for these compounds.

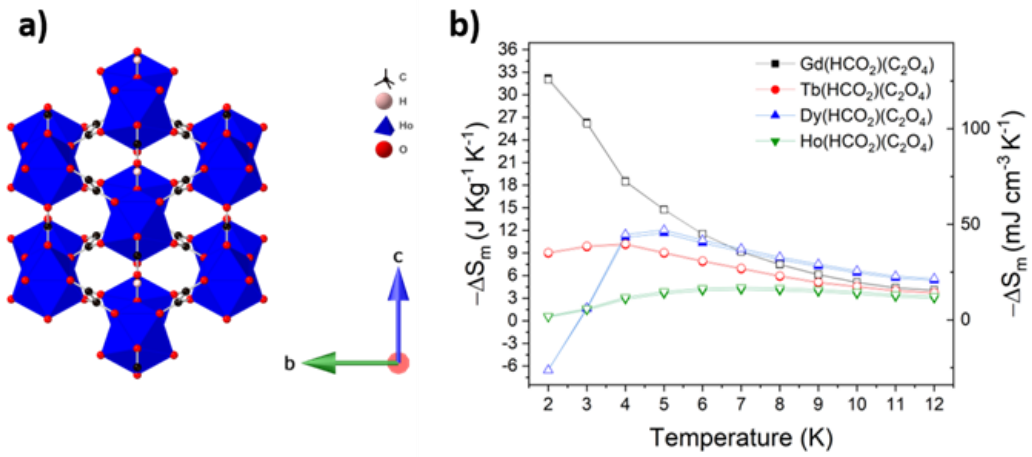

Fig. 1: a) Crystal structure of $Ho(HCO_2)(C_2O_4)$ with infinite 1-D chains arranged in a triangular lattice on the bc-plane. b) Maximum entropy change $-\Delta S_m^{max}$ for a magnetic field change of 0-2 T for members of the $Ln(HCO_2)(C_2O_4)$ family with filled and hollow symbols representing gravimetric and volumetric $-\Delta S_m^{max}$, respectively.

[1] L. Gyongyosi and S. Imre, *Comput. Sci. Rev.*, 2019, 31, 51–71.

[2] C. Mitra, *Nat. Phys.*, 2015, **11**, 212–213.

[3] A. H. Olafsdottir and H. U. Sverdrup, *Biophys. Econ. Sustain.*, 2020, **5**, 6.

[4] A. Smith, *Eur. Phys. J. H*, 2013, **38**, 507–517.

[5] G. Lorusso, J. W. Sharples, E. Palacios, O. Roubeau, E. K. Brechin, R. Sessoli, A. Rossin, F. Tuna, E. J. L. L. McInnes, D. Collison and M. Evangelisti, *Adv. Mater.*, 2013, **25**, 4653–4656.

[6] R. J. C. Dixey and P. J. Saines, *Inorg. Chem.*, 2018, **57**, 12543–12551.

[7] P. J. Saines, J. A. M. Paddison, P. M. M. Thygesen and M. G. Tucker, *Mater. Horizons*, 2015, **2**, 528–535.

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