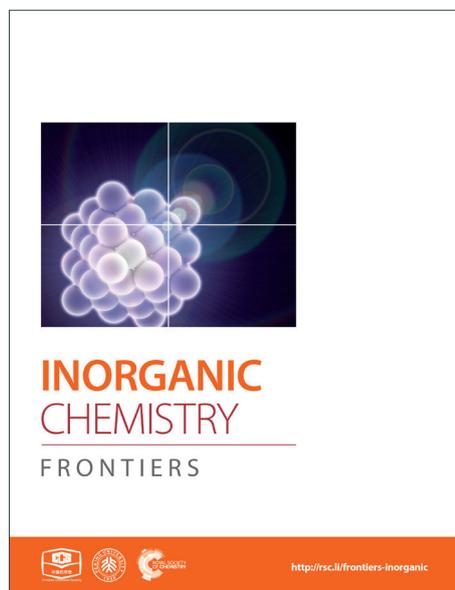
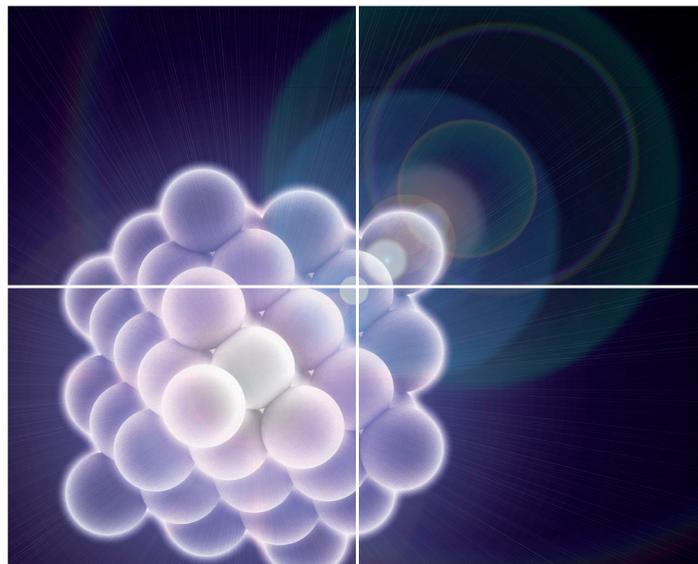


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## One-dimensional Gd<sup>III</sup>-M<sup>II</sup> (M = Mn, Co) acetate chains exhibiting large cryogenic magnetocaloric effect at $\Delta H = 3$ T

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Yin-Yin Pan, Yan Yang, La-Sheng Long\*, Rong-Bin Huang and Lan-Sun Zheng

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Two one-dimensional acetate chains, Gd<sup>III</sup>-Mn<sup>II</sup> (**1**) and Gd<sup>III</sup>-Co<sup>II</sup> (**2**), have been prepared. Magnetic investigations indicate that the magnetic entropy changes ( $-\Delta S_m$ ) in **1** have maximum values of 38.70 J kg<sup>-1</sup> K<sup>-1</sup> at  $\Delta H = 7$  T and 31.08 J kg<sup>-1</sup> K<sup>-1</sup> for  $\Delta H = 3$  T, while these in **2** have the maximum values of 35.18 J kg<sup>-1</sup> K<sup>-1</sup> at  $\Delta H = 7$  T and 28.67 J kg<sup>-1</sup> K<sup>-1</sup> at  $\Delta H = 3$  T.

Magnetocaloric effect (MCE) is a magneto-thermodynamic phenomenon in which a change in temperature of a suitable material is caused by exposing the material to a changing magnetic field.<sup>1</sup> Magnetic refrigeration is a cooling technology based on the MCE.<sup>2</sup> Owing to environmental friend and energy efficiency, magnetic refrigeration is regarded as most promising technology to replace traditional refrigeration, especially to acquire and maintain low temperature.<sup>3</sup> Although the factors influencing on the MCE of the magnetic materials have been known now, large-scale applications using magnetic refrigeration remains a great challenge. One of the obstacles to the application of the magnetic refrigeration is that the magnetic entropy of the magnetic materials synthesized so far is not large enough at a relatively low magnetic field.<sup>4</sup>

Coordination polymers, because of their structural diversity

and controllability, have recently attracted great attention in the field of magnetic refrigeration.<sup>5-8</sup> On one hand, their structural diversity and controllability facilitate us to adjust the magnetic interaction between the metal ions, leading to their MCE significantly larger than that of lanthanide alloys and magnetic nanoparticles.<sup>9-10</sup> On the other hand, when compared with metal cluster compounds, coordination polymers often possess relatively higher density, and long-range magnetic ordering,<sup>5-8</sup> resulting their MCE larger than that of metal cluster compounds.<sup>4,11</sup>

The isotropic Gd<sup>III</sup> ( $f^7$ ), and Mn<sup>II</sup> ( $d^5$ ) ions, which represent the largest magnetic entropy of cations in  $f$  and  $d$  blocks respectively, have been widely chosen to make excellent molecular cryocoolers.<sup>4b,7b,12</sup> Owing to paramagnetic or weak ferromagnetic interactions and low-lying excited spin states are of key importance for obtaining a large MCE at low magnetic field,<sup>7b</sup> all Mn<sup>II</sup> ions should be alternately separated by Gd<sup>III</sup> ions so as to avoid the relatively strong Mn<sup>II</sup>...Mn<sup>II</sup> magnetic coupling, when used Gd<sup>III</sup> and Mn<sup>II</sup> to synthesize magnetic materials. Although some Mn-Gd species with the Mn<sup>II</sup> ion alternately separated with the Gd<sup>III</sup> ion, such as, Mn<sup>II</sup><sub>4</sub>Gd<sup>III</sup><sub>6</sub>,<sup>4b</sup> Mn<sup>II</sup><sub>9</sub>Gd<sup>III</sup><sub>9</sub>,<sup>4b</sup> and Mn<sup>II</sup><sub>4</sub>Gd<sup>III</sup><sub>4</sub><sup>12</sup> clusters, have been synthesized, Mn-Gd coordination polymers with the Mn<sup>II</sup> ion alternately separated with the Gd<sup>III</sup> ion remain rare.<sup>7b</sup> Herein we report structures and MCE of two one-dimensional (1D) Gd<sup>III</sup>-M<sup>II</sup> acetate chains, formulated as [GdMn<sub>0.5</sub>(OAc)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 3H<sub>2</sub>O (**1**) and [GdCo<sub>0.5</sub>(OAc)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 3H<sub>2</sub>O (**2**). Single-crystal structural analysis reveals that the M<sup>II</sup> ions in **1** and **2** are alternately separated with the Gd<sup>III</sup> ion. Magnetic investigations indicate that the magnetic entropy is up to 31.08 J kg<sup>-1</sup> K<sup>-1</sup> for **1** and 28.67 J kg<sup>-1</sup> K<sup>-1</sup> for **2** even at  $\Delta H = 3$  T.

State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. E-mail: lslong@xmu.edu.cn

†Electronic supplementary information (ESI) available: the field dependence of magnetization for **1** and **2** at T = 2 K calculated through Brillouin function, PXRD patterns, TGA diagram and CIF files. CCDC 1006167-1006168. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

Complex **1** was prepared through the reaction of  $\text{Gd}(\text{OAc})_3 \cdot 6\text{H}_2\text{O}$  (0.388 g, 1 mmol) and  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.245 g, 1 mmol) in the mixed solution of deionized water (10 mL) and anhydrous ethanol (5 mL). Complex **2** was prepared in the similar way as described for **1**. As complexes **1** and **2** are isomorphous, only the structure of **1** is described in detail. Single-crystal structure analysis revealed that complex **1** crystallized in triclinic,  $P\bar{1}$  space group. Each asymmetric unit in **1** consists of one  $\text{Gd}^{3+}$  ion,  $0.5\text{Co}^{2+}$  ion, four acetates, two coordinated water molecules and three guest water molecules. As shown in Fig. 1, each  $\text{Gd}^{\text{III}}$  ion is located in capped square-antiprism geometry and coordinated by two water molecules, two acetates in chelate mode and three acetates in monodentate mode. Each  $\text{Mn}^{\text{II}}$  ion is located in octahedron geometry and coordinated by six acetates in monodentate mode. The two adjacent  $\text{Gd}^{\text{III}}$  ions bridged by a pair of  $\mu\text{-}\eta^2\text{:}\eta^1$  acetates, and the adjacent  $\text{Gd}^{\text{III}}$  and  $\text{Mn}^{\text{II}}$  ions bridged by one  $\mu\text{-}\eta^2\text{:}\eta^1$  acetate and two syn-syn acetates generates a 1D chain structure with each a  $\text{Mn}^{\text{II}}$  ion alternately separated with two  $\text{Gd}^{\text{III}}$  ions. This 1D chain structure is very similar to that of  $\text{NdCo}_{0.5}$ <sup>13</sup> reported previously. The bond lengths of Gd-O are 2.340(3)-2.731(3) Å, and the bond lengths of Mn-O are 2.173(3)-2.192(3) Å, which are comparable to the corresponding values in previously reported 3D Gd-Mn magnetic materials.<sup>7b,14</sup> The  $\text{Gd}\cdots\text{Gd}$  distance is 4.277(2) Å, and the Gd-O-Gd angle is 114.77(1)°, which are comparable to the corresponding values in previously reported 1D  $\text{Gd}^{3+}$  acetate chains.<sup>5b</sup> The  $\text{Gd}\cdots\text{Mn}$  distance is 4.030(6) Å, this value is smaller than the previously reported 3D Gd-Mn magnetic materials,<sup>7b,14</sup> the Gd-O2-Mn angle is 122.42(1)°. The Gd-Mn-Gd and Gd-Gd-Mn angle is 180° and 132.56(2)°, respectively. There existed intramolecular hydrogen bond between one coordination water molecule and two acetate ligands ( $\text{O}10\cdots\text{O}1 = 2.882(4)$  Å,  $\text{H}10\text{A}\cdots\text{O}1 = 2.08$  Å,  $\angle\text{O}10\text{---H}10\text{A}\cdots\text{O}1 = 157.3^\circ$ ,  $\text{O}10\cdots\text{O}6 = 2.827(4)$  Å,  $\text{H}10\text{B}\cdots\text{O}6 = 2.00$  Å,  $\angle\text{O}10\text{---H}10\text{B}\cdots\text{O}6 = 163.6^\circ$ ).

The adjacent 1D chains extends into a 2D layer structure through the water tetramer formed by two guest water molecules, O12 and O13 ( $\text{O}13\cdots\text{O}12 = 2.775(6)$  Å,  $\text{H}13\text{B}\cdots\text{O}12 = 1.88(9)$  Å,  $\angle\text{O}13\text{---H}13\text{B}\cdots\text{O}12 = 154(6)^\circ$ ), hydrogen-bonded to the carboxylate groups from adjacent chains ( $\text{O}12\cdots\text{O}3 = 2.840(4)$  Å,  $\text{H}12\text{B}\cdots\text{O}3 = 1.99$  Å,  $\angle\text{O}12\text{---H}12\text{B}\cdots\text{O}3 = 174.9^\circ$ ). Extension of the adjacent 2D layer structures through the water tetramer hydrogen-bonded to the coordinated water molecules ( $\text{O}13\cdots\text{O}9 = 2.676(5)$  Å,  $\text{H}13\text{A}\cdots\text{O}9 = 1.97$  Å,  $\angle\text{O}13\text{---H}13\text{A}\cdots\text{O}9 = 139.8^\circ$ ) from two adjacent 2D layer structures generates a 3D structure of **1** (Supporting information Fig. S1).

The bond lengths of Gd-O in **2** are 2.330(2)-2.732(2) Å, compared to these in **1**, and the bond lengths of Co-O are 2.083(2)-2.112(2) Å, the values are comparable to the previously reported ones in  $\text{NdCo}_{0.5}$  1D chain structure.<sup>13</sup> The  $\text{Gd}\cdots\text{Gd}$  distance is 4.277(9) Å, and the Gd-O-Gd angle is 114.88(8)°, comparable to those in **1**. The  $\text{Gd}\cdots\text{Co}$  distance and Gd-O-Co, Gd-Co-Gd and Gd-Gd-Co angles are 4.007(5) Å, 124.01(9)°, 180° and 132.20(2)°, respectively.

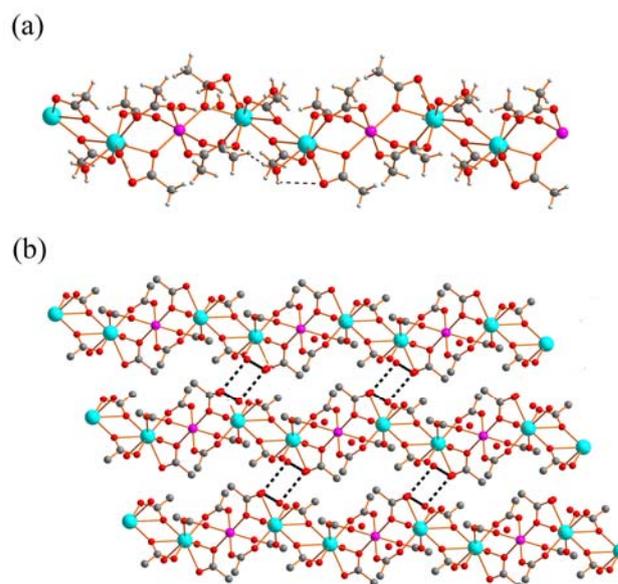


Fig. 1 (a) The 1D chain structure of **1**; (b) The 2D structure in **1**. Cyan, Gd; purple, Mn; red, O; gray, C; light gray, H; H atoms in 3D network are omitted for clarity.

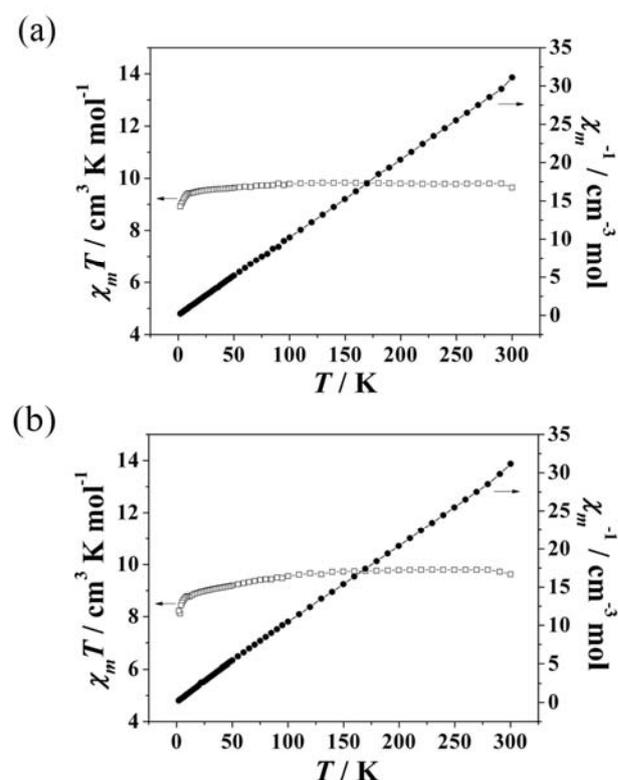
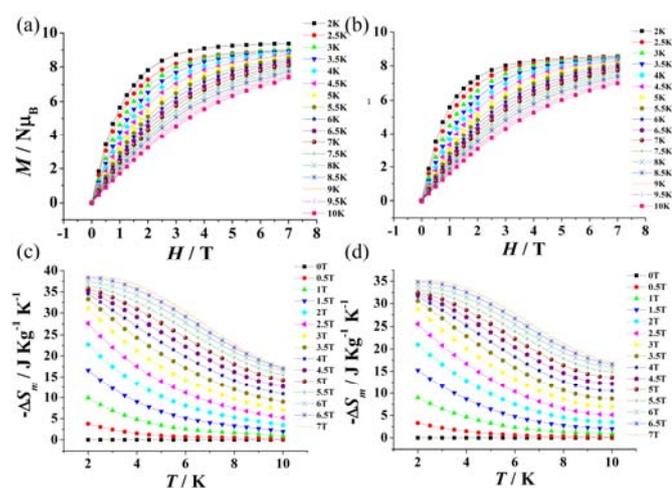


Fig. 2 Temperature dependence of the  $\chi_m T$  and the inverse molecular susceptibility plots for **1** (a) and **2** (b).

The temperature dependence of magnetic susceptibilities of **1** and **2** were measured from 2 to 300 K with an applied direct-current (dc) magnetic field of 1000 Oe. As shown in Fig. 2a and 2b, the  $\chi_m T$  value of  $9.84 \text{ cm}^3 \text{ K mol}^{-1}$  for **1** at 300 K is close to the expected spin-only value of  $10.07 \text{ cm}^3 \text{ K mol}^{-1}$  for one

isolated  $\text{Gd}^{\text{III}}$  ion ( $S = 7/2$ ,  $g = 2$ ) and 0.5 isolated  $\text{Mn}^{\text{II}}$  ion ( $S = 5/2$ ,  $g = 2$ ). With the temperature decreasing, the  $\chi_{\text{M}}T$  values remained essentially constant until 100 K, after which they decreased gradually as  $T$  decreased to 10 K, and then decreased rapidly to  $8.92 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K, probably due to the antiferromagnetic interaction of the intra-chain Gd-Gd-Mn. The  $\chi_{\text{M}}T$  value of  $8.82 \text{ cm}^3 \text{ K mol}^{-1}$  for **2** at 300 K equals to the expected spin-only value of  $8.82 \text{ cm}^3 \text{ K mol}^{-1}$  for one isolated  $\text{Gd}^{\text{III}}$  ion ( $S = 7/2$ ,  $g = 2$ ) and 0.5 isolated  $\text{Co}^{\text{II}}$  ion ( $S = 3/2$ ). With the temperature decreasing, the  $\chi_{\text{M}}T$  values stayed essentially constant until 100 K, then, they decreased gradually as  $T$  decreased to 10 K. After which, they drops rapidly to  $8.22 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K, probably ascribed to the antiferromagnetic interaction of the intra-chain Gd-Gd-Co and the zero-field splitting of the ground states.<sup>15</sup> The data obey the Curie-Weiss law with  $C = 9.804 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ,  $\theta = -0.34 \text{ K}$  for **1** and  $C = 9.901 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ,  $\theta = -2.32 \text{ K}$  for **2**. This result indicates that **1** and **2** behaved weak antiferromagnetic interactions. The stronger antiferromagnetic interaction in **2** is attributed to the anisotropy of  $\text{Co}^{\text{II}}$  ions.<sup>16</sup>



**Fig. 3** Magnetization versus applied field of **1** (a) and **2** (b) at  $T = 2$ – $10$  K and  $H = 0$ – $7$  T. Experimental  $-\Delta S_m$  obtained from magnetization data of **1** (c) and **2** (d) at various fields and temperatures.

The field dependence of magnetization of **1** and **2** was also carried out under  $T = 2$  K. As shown in Fig. 3a and 3b, the magnetization  $M$  reaches the value  $9.37 N\mu_{\text{B}}$  for **1** and  $8.42 N\mu_{\text{B}}$  for **2** respectively. The former is close to the saturated value of  $9.5 N\mu_{\text{B}}$  calculated for one isolated  $\text{Gd}^{\text{III}}$  ion ( $S = 7/2$ ) and 0.5 isolated  $\text{Mn}^{\text{II}}$  ion ( $S = 5/2$ ) in **1**, while the latter is higher than that of  $8.2 N\mu_{\text{B}}$  calculated for one isolated  $\text{Gd}^{\text{III}}$  ion ( $S = 7/2$ ) and 0.5 isolated  $\text{Co}^{\text{II}}$  ion ( $S = 1/2$ ) in **2**. The experimental value of magnetization  $M$  higher than that of the calculated one in **2** is related to the anisotropy of  $\text{Co}^{\text{II}}$  ions.<sup>16</sup> For comparison, the field dependence of magnetization for **1** and **2** at  $T = 2$  K was calculated through Brillouin function. As shown in Fig. S2 and S3 (Supporting information), the field dependence of magnetization calculated for **1** is slightly higher than that

obtained from the experimental data, while the field dependence of magnetization calculated for **2** is well consistent with that obtained from experimental data.

The magnetic entropy changes  $-\Delta S_m$  of **1** and **2** (Fig. 3c and 3d) for evaluating the MCEs can be calculated by the equation<sup>17</sup>  $\Delta S_m(T, \Delta H) = \int [\partial M(T, H) / \partial T]_H dH$  from the experimental magnetization data in Fig. 3a and 3b. The maximum value of  $-\Delta S_m$  for **1** is  $38.70 \text{ J kg}^{-1} \text{ K}^{-1}$  ( $78.68 \text{ mJ cm}^{-3} \text{ K}^{-1}$ ) at 2.5 K and  $\Delta H = 7$  T. This is smaller than the value  $48.40 \text{ J kg}^{-1} \text{ K}^{-1}$  calculated by the equation<sup>17</sup>  $-\Delta S_m = nR \ln(2S+1)$  with 1 isolated  $\text{Gd}^{\text{III}}$  ( $S = 7/2$ ) ion and 0.5  $\text{Mn}^{\text{II}}$  ( $S = 5/2$ ) ion. The maximum value of  $-\Delta S_m$  for **2** is  $35.18 \text{ J kg}^{-1} \text{ K}^{-1}$  ( $72.89 \text{ mJ cm}^{-3} \text{ K}^{-1}$ ) at 2.5 K for  $\Delta H = 7$  T, also smaller than the calculated value of  $44.93 \text{ J kg}^{-1} \text{ K}^{-1}$  with 1 isolated  $\text{Gd}^{\text{III}}$  ( $S = 7/2$ ) ion and 0.5  $\text{Co}^{\text{II}}$  ( $S = 3/2$ ) ion. The experimental maximum values of  $-\Delta S_m$  for **1** and **2** are smaller than the theoretical values probably because of the weak antiferromagnetic interactions in **1** and **2**.<sup>4c,4d</sup> Surprisingly, the MCEs can also get satisfying values of  $31.08 \text{ J kg}^{-1} \text{ K}^{-1}$  ( $63.19 \text{ mJ cm}^{-3} \text{ K}^{-1}$ ) for **1** and  $28.67 \text{ J kg}^{-1} \text{ K}^{-1}$  ( $59.40 \text{ mJ cm}^{-3} \text{ K}^{-1}$ ) for **2** even at  $\Delta H = 3$  T. These values are even higher than that for the commercial magnetic refrigerant GGG ( $-\Delta S_m \approx 24 \text{ J kg}^{-1} \text{ K}^{-1}$ , at  $\Delta H = 3$  T).<sup>18</sup> Complexes **1** and **2** exhibiting higher MCE than that of GGG at  $\Delta H = 3$  T may attributed to the weak magnetic interactions, since the magnetic interaction in GGG is paramagnetic,<sup>19</sup> while the use of paramagnetic materials as low-temperature refrigerants often requires relatively large fields to provide a relevant cooling power.<sup>20</sup>

In summary, two cheering  $3d$ - $4f$  acetate chains **1** and **2** with high MCE were reported. The MCE for complex **1** ( $-\Delta S_m = 38.70 \text{ J kg}^{-1} \text{ K}^{-1}$ ) is larger than that of **2** ( $-\Delta S_m = 35.18 \text{ J kg}^{-1} \text{ K}^{-1}$ ) at  $\Delta H = 7$  T. More importantly, the  $-\Delta S_m$  values for **1** and **2** at a lower and applicable field  $\Delta H = 3$  T are up to  $31.08 \text{ J kg}^{-1} \text{ K}^{-1}$  and  $28.67 \text{ J kg}^{-1} \text{ K}^{-1}$  respectively. The large MCE for **1** and **2** are attributed to the small acetate ligands, the increased dimension and alternate M-Gd-M structure in the complexes. The preparation of other multidimensional  $3d$ - $4f$  structures with other small-molecule ligands and alternate arrangements are in progress.

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## Notes and references

‡Synthesis of **1**:  $\text{Gd}(\text{OAc})_3 \cdot 6\text{H}_2\text{O}$  (0.388 g, 1 mmol) and  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.245 g, 1 mmol) were dissolved in a mixture of deionized water (10 mL) and anhydrous ethanol (5 mL). Then Acetic acid glacial (500  $\mu\text{L}$ , 8.75 mmol) was added while stirring, and a freshly prepared aqueous solution of NaOH (3 mL, 1.0 M) was added dropwise. The mixture was heated to  $70^\circ\text{C}$  and refluxed for 1 day. Evaporation of the filtrate under ambient conditions afforded 0.16 g of colourless cubic-shaped crystals over one month (yield 32% based on Gd).

Synthesis of **2**:  $\text{Gd}(\text{OAc})_3 \cdot 6\text{H}_2\text{O}$  (0.194 g, 0.5 mmol),  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.125 g, 0.5 mmol) were dissolved in methanol (40.0 mL), then triethylamine (0.145 mL, 1.0 mmol)

was added to it. The mixture was heated to 70 °C and refluxed for 1 day. Evaporation of the filtrate under ambient conditions afforded 0.22 g of pink cubic-shaped crystals over one month (yield 43% based on Gd).

§Crystal data for **1**: GdMn<sub>0.5</sub>C<sub>8</sub>O<sub>13</sub>H<sub>22</sub>, *M* = 510.98, triclinic, *a* = 8.2014(6) Å, *b* = 10.2761(6) Å, *c* = 11.3982(10) Å,  $\alpha$  = 111.426(7)°,  $\beta$  = 108.079(7)°,  $\gamma$  = 93.090(6)°, *V* = 834.76(11) Å<sup>3</sup>, *T* = 173 K, space group  $P\bar{1}$ , *Z* = 2, the density was 2.033 g cm<sup>-3</sup>, 3274 reflections measured, 3079 independent reflections (*R*<sub>int</sub> = 0.0314). The final *R*<sub>1</sub> value was 0.0283 (*I* > 2σ(*I*)). The final *wR*(*F*<sup>2</sup>) value was 0.0693 (*I* > 2σ(*I*)). The goodness of fit on *F*<sup>2</sup> was 1.038. Anal. Calcd for **1**: C, 18.79; H, 4.31; N, 0. Found: C, 18.73; H, 4.47; N, 0.091. IR (KBr pellet): 3405(b, s), 1552(s), 1432(s), 1384(w), 1022(w), 950(w), 676(m), 616(w).

Crystal data for **2**: GdCo<sub>0.5</sub>C<sub>8</sub>O<sub>13</sub>H<sub>22</sub>, *M* = 512.97, triclinic, *a* = 8.1656(5) Å, *b* = 10.2359(7) Å, *c* = 11.3405(6) Å,  $\alpha$  = 111.699(6)°,  $\beta$  = 108.094(5)°,  $\gamma$  = 92.947(5)°, *V* = 822.17(8) Å<sup>3</sup>, *T* = 173 K, space group  $P\bar{1}$ , *Z* = 2, the density was 2.072 g cm<sup>-3</sup>, 3218 reflections measured, 3096 independent reflections (*R*<sub>int</sub> = 0.0245). The final *R*<sub>1</sub> value was 0.0203 (*I* > 2σ(*I*)). The final *wR*(*F*<sup>2</sup>) value was 0.0516 (*I* > 2σ(*I*)). The goodness of fit on *F*<sup>2</sup> was 1.030. Anal. Calcd for **2**: C, 18.71; H, 4.29; N, 0. Found: C, 18.67; H, 4.32; N, 0.800. IR (KBr pellet): 3392(b, s), 1547(s), 1428(s), 1384(w), 1029(w), 952(w), 680(m), 619(w).

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