

# Novel three-dimensional 3d–4f microporous magnets exhibiting selective gas adsorption behavior†

Cui-Jin Li,<sup>a</sup> Zhuo-jia Lin,<sup>a</sup> Meng-Xia Peng,<sup>ab</sup> Ji-Dong Leng,<sup>a</sup> Ming-Mei Yang<sup>ac</sup> and Ming-Liang Tong<sup>\*a</sup>

Received (in Cambridge, UK) 28th August 2008, Accepted 24th September 2008

First published as an Advance Article on the web 29th October 2008

DOI: 10.1039/b815024a

**Three microporous Ln-Co-pyta heterometallic compounds [Ln<sub>4</sub>Co<sub>3</sub>(pyta)<sub>6</sub>(H<sub>2</sub>O)<sub>9</sub>·5H<sub>2</sub>O (Ln = Sm (1), Eu (2), Gd (3); H<sub>3</sub>pyta = 2,4,6-pyridinetricarboxylic acid) have interesting selective adsorption abilities towards H<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub> because of size-selective effects; magnetic analysis reveals that 3 has a ferromagnetic behavior.**

Multifunctional molecular materials, such as porous magnets, are currently provoking great interest due to their synergism of magnetic and porous properties,<sup>1–4</sup> which have promising applications in storage, catalysis and separation<sup>5–7</sup> as porous molecule magnet materials. Many fascinating dynamic magnetic behaviors, *e.g.* solvatomagnetic effects,<sup>8,9</sup> have been observed in porous magnets. However, it is a great challenge to design crystalline materials, especially heterometallic compounds, combining porosity and interesting magnetic properties. Herein we report the synthesis, structures, adsorption and magnetic properties of three new microporous compounds [Ln<sub>4</sub>Co<sub>3</sub>(pyta)<sub>6</sub>(H<sub>2</sub>O)<sub>9</sub>·5H<sub>2</sub>O (Ln = Sm (1), Eu (2) and Gd (3); H<sub>3</sub>pyta = 2,4,6-pyridinetricarboxylic acid).

Heterometallic complexes containing both d-block transition and f-block lanthanide metal ions have been intensively investigated because of their fascinating structural diversity, and interesting applications as unique magnetic and optical materials.<sup>10</sup> The difficulty of obtaining and controlling high-dimensional mixed lanthanide–transition metal organic coordination frameworks (MOF) may be attributed to the fact that d- and f-block ions have distinctly different chemical and coordination behaviors.<sup>11</sup> To our knowledge, most studies on exchange coupled systems with three-dimensional (3D) 3d–4f MOF structures have been Ln(III)–Cu(II) systems,<sup>11</sup> with examples of other Ln(III)–transition metal ion systems being much less well documented,<sup>12</sup> though several 3D 3d–4f molecular materials have been reported so far.<sup>13</sup> It remains a great challenge to achieve a better understanding of the magnetic

interactions that involve 3d–4f couples. The major difficulties arise from the combined effects of the crystal field and the orbital contribution of the Ln<sup>3+</sup> ion, which can result in an important anisotropy of the magnetic susceptibility and the exchange interaction.<sup>11</sup>

A reaction of Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and H<sub>3</sub>pyta in distilled water (10 mL) in the molar ratio 2 : 5 : 10 under hydrothermal conditions at 180 °C for 4 d resulted in three heterometallic isomorphous compounds, 1–3 (see ESI†), which were characterized by single crystal X-ray unit cell determination, IR spectra, powder X-ray diffraction (PXRD) and elemental analysis (Fig. S1†). The isostructural frameworks in 1–3 come from their analogous coordination behaviour and the almost identical ionic radii of Sm, Eu and Gd. Similar effects have been found in our previous work.<sup>14</sup>

The structure of 2 was fully analyzed by single crystal X-ray crystallography. There are two crystallographically independent Co(II) atoms in a distorted octahedral geometry, three unique Eu(III) atoms, and three pyta<sup>3–</sup> ligands in μ<sub>4</sub>- and μ<sub>5</sub>-bridging modes in the asymmetric unit (Fig. 1). One of the cobalt atoms (Co2) and two of the europium atoms (Eu2 and Eu3) are situated on two-fold screw axes. Co1 is chelated by two pyta<sup>3–</sup> ligands (ONO) *via* the 2- and 6-carboxylates, and the pyridine group, while Co2 is surrounded by four disordered water molecules in the equatorial plane and two 6-carboxylate oxygen atoms from two pyta<sup>3–</sup> ligands in the axial positions. Eu1 is in a nine-coordinate mono-capped square antiprism geometry connected to one water molecule and five pyta<sup>3–</sup> ligands *via* one pyridine nitrogen and seven O<sub>carboxyl</sub> atoms (Fig. S2(a)†). Eu2 is coordinated to eight O<sub>carboxyl</sub> atoms from six pyta<sup>3–</sup> ligands in a distorted square antiprism

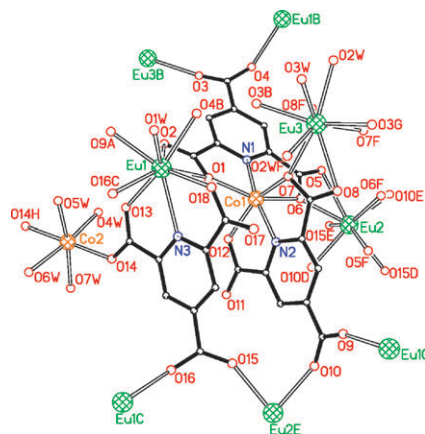


Fig. 1 The coordination environment of Eu and Co atoms in 2.

<sup>a</sup> MOE Key Laboratory of Bioinorganic and Synthetic Chemistry/State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, 510275 Guangzhou, P. R. China. E-mail: tongml@mail.sysu.edu.cn

<sup>b</sup> Department of Chemistry, Jiaying University, 514015 Meizhou, P. R. China

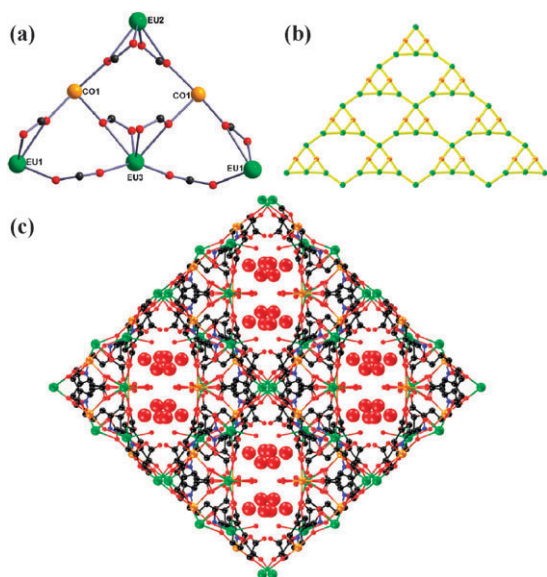
<sup>c</sup> Department of Chemistry, Guangxi Teachers Education University, 530000 Nanning, P. R. China

† Electronic supplementary information (ESI) available: Synthesis, crystallographic details, VPXRD pattern and TGA. CCDC 700258 contains the crystallographic data of 2 for this paper (see ESI). See DOI: 10.1039/b815024a

geometry (Fig. S2(b)†). The coordination geometry for the nine-coordinate Eu3 atom is a distorted tri-capped trigonal prism, which is surrounded by three O<sub>aqua</sub> and six O<sub>carboxyl</sub> atoms from five pyta<sup>3-</sup> ligands (Fig. S2(c)†).

As the carboxylate groups on the 2- and 6-positions of the pyta<sup>3-</sup> ligands chelated to Co1 are further connected to one and two lanthanide ions, respectively, the Co1(pyta)<sub>2</sub><sup>4-</sup> units can be considered as multidentate metallogligands that link neighbouring Eu ions to form a trigonal Eu<sub>4</sub>Co<sub>2</sub>(COO)<sub>8</sub> building unit (Fig. 2(a)). The two-fold screw axis runs along the direction of the Eu2 and Eu3 atoms (Eu1–Co1 4.507(4), Eu2–Co1 4.615(9), Eu3–Co1 4.534(4), Eu1–Eu3 5.78(1) Å). Each Eu<sub>4</sub>Co<sub>2</sub>(COO)<sub>8</sub> unit is connected to six adjacent units by three Co2(H<sub>2</sub>O)<sub>4</sub>(pyta)<sub>2</sub><sup>4-</sup> units and eight bridging carboxylate groups to form a mixed lanthanide cobalt carboxylate layer in the *ab* plane (Fig. 2(b) and Fig. S3†). The 4-carboxylates from the Co1(pyta)<sub>2</sub><sup>4-</sup> and Co2(H<sub>2</sub>O)<sub>4</sub>(pyta)<sub>2</sub><sup>4-</sup> metallogligands bridge the Eu atoms of neighbouring layers to construct a 3D coordination framework with 1D ellipsoid channels along the *c* axis (Fig. 2(c)). All coordinated water and unbonded carboxylate oxygen atoms point towards the channels, forming hydrophilic cavities filled with guest water molecules. Each channel is divided by water ligands on the Co2 atoms into two parts of size 2.5 × 3.5 Å. The void volume of the channels without the guest molecules, calculated by PLATON, is 16.5%.

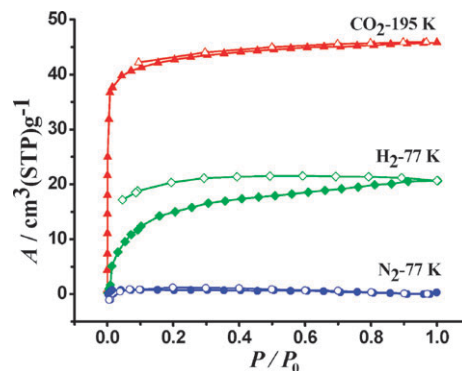
**1–3** had similar thermal stabilities, as measured by thermogravimetric analysis (TGA). For compound **1**, the first weight loss of 3.95% (calc. 3.94%) occurred below 95 °C, corresponding to the loss of five guest water molecules. The nine coordinated water molecules were released between 95 and 280 °C (weight loss observed 7.10%, calc. 7.11%). The compound began to decompose at above 500 °C. Variable-temperature X-ray powder diffraction showed that the framework was retained until 210 °C (Fig. S5†).



**Fig. 2** (a) The butterfly-like Eu<sub>4</sub>Co<sub>2</sub>(COO)<sub>8</sub> unit and (b) the 2D carboxylate-bridged Eu<sub>4</sub>Co<sub>2</sub> layer in **2**. (c) Top view of the 3D microporous MOF of **2**. Green, Eu; orange, Co; red, O; black, C; blue, N. Hydrogen atoms are omitted for clarity. Guest water molecules in the channels are amplified.

The gas adsorption properties towards small molecules, *i.e.* N<sub>2</sub>, H<sub>2</sub> and CO<sub>2</sub>, were investigated for **1**. Desolvated **1** was obtained by heating at 120 °C in a high vacuum for 3 h. As showed in Fig. 3, the adsorption isotherm for desolvated **1** revealed very little N<sub>2</sub> (77 K) uptake. Surprisingly however, a significant amount of H<sub>2</sub> (77 K) and CO<sub>2</sub> (195 K) adsorption was observed. The uptake amounts for H<sub>2</sub> and CO<sub>2</sub> at 1.0 atm were 20 and 45 cm<sup>3</sup> g<sup>-1</sup>, respectively. The results for the selectivity of H<sub>2</sub> over N<sub>2</sub> at 77 K were as expected for size exclusion reasons (kinetic diameter: 2.89 Å for H<sub>2</sub> vs. 2.99 Å for N<sub>2</sub>),<sup>15</sup> the low thermal energy of the framework, and the low kinetic energy of the N<sub>2</sub> and H<sub>2</sub> molecules, resulting in a hindered diffusion. More interestingly, the isotherms measured at 77 K revealed the formation of hysteresis loops for H<sub>2</sub> adsorption, which have recently been observed as an unusual behavior by Navarro *et al.*<sup>15a</sup> Such desorption kinetics might also be related to the structural features of desolvated **1** with unsaturated metal centres, since the system retained some crystallinity after the removal of the coordinated water molecules according to thermal XRPD, whereas the favoured diffusion of the slightly larger CO<sub>2</sub> molecules (3.189 Å) at 195 K should be related to both the flexibility of the framework at higher temperatures and the resulting higher kinetic energy of the CO<sub>2</sub> molecules.<sup>15</sup> The shape of the isotherm was fully reversible and is typical of molecular sieves, with a steep rise at low pressure that is consistent with the micropores in the framework. The surface area, estimated through the adsorption isotherm of CO<sub>2</sub>, was 237 m<sup>2</sup> g<sup>-1</sup> by the Langmuir equation.

The temperature dependence of the magnetic susceptibilities of **1–3** were examined in the temperature range 2–300 K at a direct current field of 1.0 kOe (Fig. 4). The  $\chi_{MT}$  value for **1** was 10.42 cm<sup>3</sup> K mol<sup>-1</sup> at room temperature, significantly higher than the expected value of 5.98 cm<sup>3</sup> K mol<sup>-1</sup> for the isolated contribution from three high-spin Co(II) ions ( $S = 3/2$ ,  $g_{Co} = 2.0$ ) and four Sm(III) ions ( $J = 5/2$ ,  $g_J = 2/7$ ).<sup>16</sup> Upon cooling, the  $\chi_{MT}$  value monotonically decreased to 5.23 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K. The trend of the magnetization curve for **2** was similar to that of **1**. The experimental  $\chi_{MT}$  value at room temperature for **2** was 14.90 cm<sup>3</sup> K mol<sup>-1</sup>, considerably higher than the expected value of 11.63 cm<sup>3</sup> K mol<sup>-1</sup> for four magnetically non-interacting Eu(III) ions, calculated by Van Vleck, allowing for the population of the excited state with higher values of  $J$ <sup>17</sup> ( $J = 3.0$ ,  $g_J = 1.0$ ), and three isolated high-spin Co(II) ions ( $S = 3/2$ ,  $g_{Co} = 2.0$ ). The  $\chi_{MT}$  decreases



**Fig. 3** Adsorption isotherms of CO<sub>2</sub> (▲) at 195 K, and H<sub>2</sub> (◆) and N<sub>2</sub> (●) at 77 K for dehydrated **1**. The open symbols denote desorption.

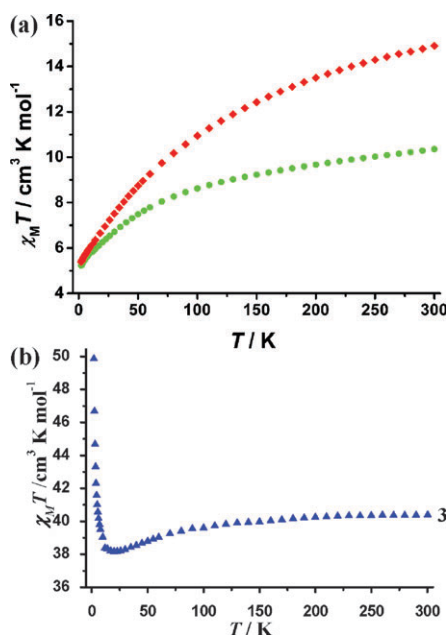


Fig. 4 Plots of  $\chi_M T$  vs.  $T$  for (a) **1** (◆), **2** (●) and (b) **3** (▲) at 1.0 kOe.

continuously with the temperature to  $5.38 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K. The decrease in  $\chi_M T$  values at low temperature for **1** and **2** might be attributed to the combined effect of the single ion behavior of high-spin Co(II) ions<sup>18</sup> and the splitting of the ligand field of the lanthanide ions because of strong spin-orbital coupling. The magnetic behaviors of the 3d-4f system correspond to both magnetic coupling of the paramagnetic metal centers and strong spin-orbit coupling of the lanthanide ions,<sup>16,19</sup> which are especially complicated in multi-dimensional structures. Thus, the coupling interactions between Ln-Co (Ln = Sm (**1**) and Eu (**2**)) in the 3D MOFs of **1** and **2** are not explicitly characterized.

The overall magnetic behavior of **3** showed ferromagnetic interactions between adjacent Gd···Gd and Gd···Co centers in the 3D covalent structure. The observed  $\chi_M T$  value of **3** at room temperature was  $40.40 \text{ cm}^3 \text{ K mol}^{-1}$ , slightly larger than the  $37.13 \text{ cm}^3 \text{ K mol}^{-1}$  expected for four isolated Gd(III) ions ( $S = 7/2$ ,  $g_{\text{Gd}} = 2.0$ ; with the ground state  $^8S_{7/2}$ )<sup>16</sup> and three magnetically-uncorrelated Co(II) ions ( $S = 3/2$ ,  $g_{\text{Co}} = 2.0$ ). The  $\chi_M T$  decreased steadily from 300 K and reached a minimum  $38.16 \text{ cm}^3 \text{ K mol}^{-1}$  at ca. 20 K. Upon further cooling, a sharp increase was observed. The  $\chi_M T$  value at ca. 2 K was  $49.86 \text{ cm}^3 \text{ K mol}^{-1}$ . Magnetization measurements in the 0–7 T range at 2 K also supported the occurrence of intralayer ferromagnetic Gd···Gd/Co interactions in **3** (Fig. S6(c)†). The experimental curve gradually approached the calculated M/H value of the coupled  $S = 37/2$  state ( $S_{\text{Gd}} = 7/2$ ,  $g_{\text{Gd}} = 2.0$ ;  $S_{\text{Co}} = 3/2$ ,  $g_{\text{Co}} = 2.0$ ). It should be noted that compounds for which Gd(III) has exchange interactions with other paramagnetic metal ions are relatively undocumented,<sup>11a</sup> and the exchange interactions in most homopolynuclear gadolinium complexes reported so far are weak and antiferromagnetic,<sup>11a</sup> except for dimeric  $[\text{Gd}_2(\text{salicylate})_6(\text{H}_2\text{O})_2]$ , in which a ferromagnetic Gd(III)–Gd(III) interaction was found.<sup>20</sup> The occurrence of ferromagnetic Gd···Gd/Co interactions in **3** may result from the non-coplanar  $\mu_{1,2}$ -carboxylato and monoatom oxygen bridges.

In summary, we have synthesized three stable 3D Ln–Co coordination polymers with hydrophilic channels that exhibit a size-selective adsorption ability for  $\text{H}_2$  and  $\text{CO}_2$  over  $\text{N}_2$ . The magnetic behaviors of three isomorphous compounds, **1–3**, have provided useful information for future magnetostructural correlation analyses of 3d–4f systems.

This work was supported by the NSFC (no. 20525102, 20821001 and 50872157) and the “973 Project” (2007CB815305).

## Notes and references

- (a) Z. M. Wang, Y. J. Zhang, T. Liu, M. Kurmoo and S. Gao, *Adv. Funct. Mater.*, 2007, **17**, 1523; (b) D. Maspoch, D. Ruiz-Molina and J. Veciana, *J. Mater. Chem.*, 2004, **14**, 2713; (c) C. J. Kepert, *Chem. Commun.*, 2006, 695.
- (a) M. Kurmoo, H. Kumagai, M. Akita-Tanaka, K. Inoue and S. Takagi, *Inorg. Chem.*, 2006, **45**, 1627; (b) V. Niel, A. L. Thompson, M. C. Muñoz, A. Galet, A. E. Goeta and J. A. Real, *Angew. Chem., Int. Ed.*, 2003, **42**, 3760.
- K. Barthelet, J. Marrot, D. Riou and G. Férey, *Angew. Chem., Int. Ed.*, 2002, **41**, 281.
- S.-C. Xiang, X.-T. Wu, J.-J. Zhang, R.-B. Fu, S.-M. Hu and X.-D. Zhang, *J. Am. Chem. Soc.*, 2005, **127**, 16352.
- J.-R. Li, Y. Tao, Q. Yu, X.-H. Bu, H. Sakamoto and S. Kitagawa, *Chem.–Eur. J.*, 2008, **14**, 2771.
- M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469.
- (a) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040; (b) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, R. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe and Y. Mita, *Nature*, 2005, **436**, 238.
- G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray and J. D. Cashion, *Science*, 2002, **298**, 1762.
- (a) M. Kurmoo, H. Kumagai, K. W. Chapman and C. J. Kepert, *Chem. Commun.*, 2005, 3012; (b) D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira and J. Veciana, *Nat. Mater.*, 2003, **2**, 190.
- T. K. Prasad, M. V. Rajasekharan and J.-P. Costes, *Angew. Chem., Int. Ed.*, 2007, **46**, 2851.
- (a) *Magnetism: Molecules to Materials V*, ed. J. S. Miller and M. Drillon, Wiley-VCH Verlag GmbH, Weinheim, Germany, 2005 ch. 5, p. 161; (b) S. Xiang, S. Hu, T. Sheng, R. Fu, X. Wu and X. Zhang, *J. Am. Chem. Soc.*, 2007, **129**, 15144.
- (a) H.-Z. Kou, B. C. Zhou, S. Gao and R.-J. Wang, *Angew. Chem., Int. Ed.*, 2003, **42**, 3288; (b) T. Shiga, H. Okawa, S. Kitagawa and M. Ohba, *J. Am. Chem. Soc.*, 2006, **128**, 16426.
- (a) H.-L. Sun, H. Shi, F. Zhao, L. Qi and S. Gao, *Chem. Commun.*, 2005, 4339; (b) B. Zhao, X. Y. Chen, P. Cheng, D. Z. Liao, S. P. Yan and Z. H. Jiang, *J. Am. Chem. Soc.*, 2004, **126**, 15394; (c) O. Guillou, C. Daiguebonne, M. Camara and N. Kerbellec, *Inorg. Chem.*, 2006, **45**, 8468; (d) H. B. Cui, B. Zhou, L. S. Long, Y. Okano, H. Kobayashi and A. Kobayashi, *Angew. Chem., Int. Ed.*, 2008, **47**, 3376; (e) Y. Zhou, M. Hong and X. Wu, *Chem. Commun.*, 2006, 135.
- C.-J. Li, M.-X. Peng, J.-D. Leng, M.-M. Yang, Z.-J. Lin and M.-L. Tong, *CrystEngComm*, 2008, 1645.
- (a) J. A. R. Navarro, E. Barea, A. Rodríguez-Diéguez, J. M. Salas, C. O. Ania, J. B. Parra, N. Masciocchi, S. Galli and A. Sironi, *J. Am. Chem. Soc.*, 2008, **130**, 3978; (b) X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw and M. J. Rosseinsky, *Science*, 2004, **306**, 1012.
- C. Benelli and D. Gatteschi, *Chem. Rev.*, 2002, **102**, 2369.
- Y. H. Wan, L. P. Zhang, L. P. Jin, S. Gao and S. Z. Lu, *Inorg. Chem.*, 2003, **42**, 4985.
- R. L. Carlin, *Magnetochemistry*, Springer, Berlin, 1986.
- (a) Y.-Q. Sun, J. Zhang, Y.-M. Chen and G.-Y. Yang, *Angew. Chem., Int. Ed.*, 2005, **44**, 5814; (b) B. Ma, D. Zhang, S. Gao, T. Jin, C. Yan and G. Xu, *Angew. Chem., Int. Ed.*, 2000, **39**, 3644.
- J.-P. Costes, J. M. Clemente-Juan, F. Dahan, F. Nicodème and M. Verelst, *Angew. Chem., Int. Ed.*, 2002, **41**, 323.