

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

The Ln-Cu(II)-Hpic-H₂BDC system showing interesting production variety upon different reaction conditions: hydrothermal synthesis, structures, thermostability, and magnetism

Feng Luo^a; Ming-Biao Luo^a; Xiao-Lan Tong^a

^a College of Biology, Chemistry and Material Science, East China Institute of Technology, Fuzhou, Jiangxi, China

First published on: 07 April 2010

To cite this Article Luo, Feng , Luo, Ming-Biao and Tong, Xiao-Lan(2010) 'The Ln-Cu(II)-Hpic-H₂BDC system showing interesting production variety upon different reaction conditions: hydrothermal synthesis, structures, thermostability, and magnetism', *Journal of Coordination Chemistry*, 63: 7, 1147 — 1156, First published on: 07 April 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958971003759093

URL: <http://dx.doi.org/10.1080/00958971003759093>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Ln–Cu(II)–Hpic–H₂BDC system showing interesting production variety upon different reaction conditions: hydrothermal synthesis, structures, thermostability, and magnetism

FENG LUO*, MING-BIAO LUO and XIAO-LAN TONG

College of Biology, Chemistry and Material Science, East China Institute of Technology, Fuzhou, Jiangxi, China

(Received 15 October 2009; in final form 23 December 2009)

Herein, we report research regarding the Ln–Cu(II)–Hpic–H₂BDC system, where Ln, Hpic, and H₂BDC are lanthanide ions, picolinic acid, and 1,2-benzenedicarboxylic acid, respectively. Under different reaction temperatures (160°C and 170°C), the self-assembly of Gd₂O₃, CuCl₂, Hpic, and H₂BDC in water at pH = 2 adjusted by HClO₄ generates two Ln-containing coordination compounds, GdCu(pic)(PhCOO)₄ (**1**) and Gd(pic)(BDC)(μ-H₂O)₂(H₂O) (**2**) (PhCOOH = benzenecarboxylic acid). Under the same reaction conditions, if Gd₂O₃ is replaced by Pr₃O₄, then polymer Pr₄(BDC)₆(μ-H₂O)₂ (**3**) is obtained. The structural features are 1-D tape or 2-D irregular (6, 3) net. We also explored their phase purity by X-ray diffraction analysis and evaluated their thermostability by thermogravimetric analysis studies.

Keywords: Coordination compound; Hydrothermal synthesis; (6, 3) Net

1. Introduction

Lanthanide-based metal–organic frameworks (MOFs) have unusual coordination characteristics and exceptional optical and magnetic properties. Compared to transition metals, lanthanides have much higher coordination numbers and more flexible coordination geometry, making it difficult to control the preparation of lanthanide complexes but giving unusual MOF architectures. Many 3d–4f coordination polymers have been reported [1], possessing interesting structural motifs and significant properties such as chemical sensors [2], fluorescence [3], and catalysis [4]. Their magnetic properties have also attracted attention owing to the unique 3d–4f magnetic exchange interactions [5]. To generate target 3d–4f coordination polymers by design, a judicious choice of ligands is the key. A typical strategy is self-assembly from mixed-metal ions and ligands such as pyridinecarboxylate [6]. Picolinic acid (Hpic) has been widely used to construct 3d coordination polymers [7]. By contrast, pic-based 4f or 3d–4f complexes are rare [8]. In 2005, Guo *et al.* [8c] pioneered the research of the

*Corresponding author. Email: ecit.luofeng@gmail.com

Cu(II)–4f–Hpic system, and several Cu(II)–4f–pic compounds were prepared with 1-D chains and 2-D layers. As an ongoing research toward the rational design and preparation of 3d–4f complexes [9]; herein, we report Cu(II)–4f–Hpic system into the Cu(II)–4f–Hpic–H₂BDC system because the introduction of H₂BDC co-ligand can generate new 3d–4f compounds with intriguing framework architectures. By contrast to the reported Cu(II)–4f–Hpic system, the present system is difficult, as there exists coordination competition between 3d and 4f metals with Hpic and H₂BDC ligands. The detailed hydrothermal synthesis, structure, X-ray diffraction (XRD), and thermogravimetric analysis (TG) studies are listed below.

2. Experimental

2.1. Materials and methods

All reagents were purchased from commercial sources without purification. Analyses for C, H, and N were carried out on a Perkin Elmer analyzer. Elemental analysis for C, H, and N was performed on a Perkin Elmer 240 analyzer. The TG was investigated at 30°C–800°C on a standard TG analyzer under a nitrogen flow at a heating rate of 5°C min⁻¹ for all measurements.

2.2. Synthesis of 1–3

2.2.1. Synthesis of GdCu(pic)(PhCOO)₄ (1). A mixture of Gd₂O₃, CuCl₂, Hpic, and H₂BDC in 10 mL deionized water in the ratio of 1:1:2:1 was adjusted by HClO₄ solution to pH = 2. The mixture was sealed and placed in a 25 mL Teflon-lined reactor and heated at 170°C for 3 days, then cooled slowly to room temperature with blue single crystals of **1** obtained (yield *ca* 63%, based on H₂BDC). Elemental analysis for **1** (%): Calcd: C 49.34, H 2.92, and N 1.69; Found: C 49.35, H 2.98, and N 1.66. The phase purity of the crystalline materials is confirmed by powder XRD.

2.2.2. Synthesis of Gd(pic)(BDC)(μ-H₂O)₂(H₂O) (2). A mixture of Gd₂O₃, CuCl₂, Hpic, and H₂BDC in 10 mL deionized water in the ratio of 1:1:2:1 was adjusted by HClO₄ solution to pH = 2. The mixture was sealed and placed in a 25 mL Teflon-lined reactor and heated at 160°C for 3 days, then cooled slowly to room temperature giving colorless single crystals of **2** (yield *ca* 68%, based on Gd). Elemental analysis for **2** (%): Calcd: C 33.79, H 2.84, and N 2.82; Found: C 33.81, H 2.86, and N 2.84. The phase purity of the crystalline materials is confirmed by XRD.

2.2.3. Synthesis of Pr₄(BDC)₆(μ-H₂O)₂ (3). A mixture of Pr₃O₄, CuCl₂, Hpic, and H₂BDC in 10 mL deionized water in the ratio of 1:1:2:1 was adjusted by HClO₄ solution to pH = 2. The mixture was sealed and placed in a 25 mL Teflon-lined reactor and heated at 170°C for 3 days, then cooled slowly to room temperature and aqua single crystals of **3** were obtained (yield *ca* 81%, based on H₂BDC). Elemental analysis

for **3** (%): Calcd: C 36.38 and H 1.78; Found: C 36.41 and H 1.79. The phase purity of the crystalline materials is confirmed by XRD.

2.3. Crystallographic measurements on 1–3

Suitable single crystals of **1–3** were selected and mounted in air onto thin glass fibers. Accurate unit cell parameters were determined by a least-squares fit of 2θ values and intensity data were measured on a Bruker CCD area diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The intensities were corrected for Lorentz and polarization effects as well as for empirical absorption based on multiscan technique; all structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97. All nonhydrogen atoms were refined with anisotropic thermal parameters. Crystallographic data for the three compounds are summarized in table 1 (Supplementary material).

3. Results and discussion

3.1. Synthesis

Compound **1** was obtained by hydrothermal reaction (at 170°C) of Gd₂O₃, CuCl₂, Hpic, H₂BDC, and HClO₄ (used to adjust the pH = 2) in the ratio of 1 : 1 : 2 : 1. In this reaction, HClO₄ plays the role to adjust the pH but cannot be replaced with HCl, H₂SO₄, or HNO₃ as no product was obtained. At high temperature, the original H₂BDC was decomposed to PhCOOH; hence, we tried a lower reaction temperature (160°C), but only **2** was obtained, where the original H₂BDC was not decomposed [10].

Table 1. Crystallographic data and structure refinement details for **1–3**.

	1	2	3
Empirical formula	C ₃₄ H ₂₄ CuGdNO ₁₀	C ₁₄ H ₁₄ GdNO ₉	C ₄₈ H ₂₈ O ₂₆ Pr ₄
Formula weight	827.33	497.51	1584.35
Temperature (K)	293(2)	294(2)	293(2)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2(1)/c$	$P1$
Unit cell dimensions (Å, °)			
<i>a</i>	11.251(2)	14.721(2)	7.8789(16)
<i>b</i>	11.554(2)	6.1123(9)	11.564(2)
<i>c</i>	12.185(2)	22.585(3)	15.046(3)
α	81.72(3)	90	111.45(3)
β	84.72(3)	128.369(6)	95.57(3)
γ	82.70(3)	90	101.54(3)
Volume (Å ³), <i>Z</i>	1550.4(5), 2	1593.3(4), 4	1228.2(4), 1
Calculated density (g cm ⁻³)	1.772	2.074	2.137
<i>S</i>	1.026	1.013	1.041
Flack factor			−0.008(18)
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0307, <i>wR</i> ₂ = 0.0621	<i>R</i> ₁ = 0.0252, <i>wR</i> ₂ = 0.0604	<i>R</i> ₁ = 0.0364, <i>wR</i> ₂ = 0.0983

Under the same reaction conditions (at 160°C or 170°C), the substitution of Gd by Pr did not give isostructural compound.

3.2. Description of crystal structures

3.2.1. GdCu(pic)(PhCOO)₄ (1). The single crystal XRD analysis shows *P-1*, triclinic space group for **1**. Cu1 and Cu2 were located on an inversion center with four-coordinate CuO₄ and CuO₂N₂ square geometry completed by PhCOO⁻ and pic⁻ N/O, respectively. The Cu–O bond lengths in the range 1.930–1.962 Å are comparable with the Cu–N bond lengths of 1.948 Å. Gd1 is surrounded by six PhCOO⁻ and one pic⁻ oxygen, leading to monocapped trigonal-prism geometry (figure 1a). The Gd–O bond lengths vary from 2.293 to 2.409 Å, comparable to other Gd(III)-containing compounds [5, 6]. Based on the balance of charge and coordination environment of copper together with bond-valence calculation (the bond-valence parameter is *ca* 1.9 for Cu1 and 1.8 for Cu2) [11], we know that copper is divalent. The carboxylate of pic⁻ and PhCOO⁻ are bidentate.

As illustrated in figure 1(a), Cu1 and Gd1 are alternately connected, –Cu–Gd–Gd–Cu–, to give infinite CuGd₂(CO₂)₈ rod-shaped heterometallic carboxylate substructure, where the closest Cu–Gd and Gd–Gd distances are 4.292 and 4.305 Å, respectively (figure 2a). Several discrete rod-shaped heterometallic (3d–4f) carboxylate substructures have been reported [9b], but such special rod-like substructure is undeveloped. Furthermore, these substructures are integrated by Cu(pic)₂ units, resulting in the 2-D honeycomb network (figure 2c). In each single (6,3) net, the Gd···Gd···Gd angles are from 64.618° to 153.699°, while the adjacent Gd(III)–Gd(III) distances vary from 4.305 to 11.831 Å. Similar Pr₆ (6,3) sheets have been observed in one Pr-containing homometallic coordination polymer [12], but such 3d–4f heterometallic honeycomb network is uncommon. In addition, significant π – π interactions (PhCOO⁻-to-PhCOO⁻/3.637 Å) are observed between layers and the interlayer distance is *ca* 11.5 Å.

3.2.2. Gd(pic)(BDC)(μ -H₂O)₂(H₂O) (2). Under the same reaction conditions as **1**, if the reaction temperature is 160°C, then **2** is the only product. Compound **2** crystallizes in *P2₁/c*, monoclinic space group. In **2**, the Gd(III) centers are nine-coordinate, tricapped trigonal-prism geometry (figure 1b), completed by one pic⁻ providing one nitrogen and one oxygen, three BDC²⁻ ligands giving six oxygens as well as two

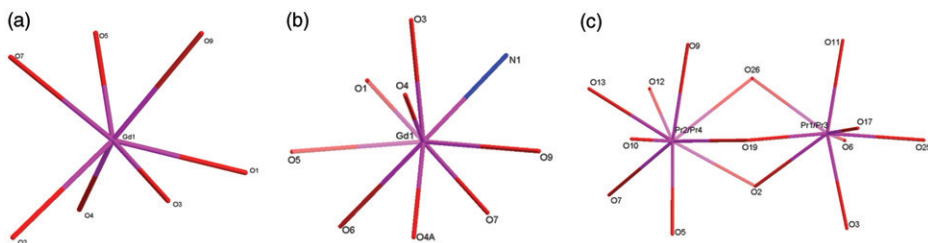


Figure 1. The coordination geometry of Gd in **1–2** and Pr in **3**.

terminal waters. The Gd–O bond lengths vary from 2.345 to 2.699 Å in the normal range [5, 6]. The carboxylate of pic[−] is monodentate, while those of BDC^{2−} are chelate and $\mu_2:\eta^2:\eta^1$ coordinated.

Gd1 and the symmetry-related Gd1A are bridged by two μ_2 -O of BDC^{2−} to generate the binuclear Gd₂ fragment with Gd–Gd distance of 4.295 Å and Gd–(μ_2 -O)–Gd angle of 113.99°. Along *b*, these fragments are linked by BDC^{2−} to 1-D tape-like configuration (figure 3). Along *c*, these 1-D structures are separated by *ca* 8.7 Å, and in turn linked by hydrogen bonds.

3.2.3. Pr₄(BDC)₆(μ -H₂O)₂ (3). Single crystal XRD analysis of **3** suggests the chiral space group *P1* with the Flack factor of −0.008(18). In **3**, there are four independent Pr(III) with two different coordination geometries (figure 1c). Pr1 and Pr3 have bicapped trigonal-prism geometry, furnished by seven BDC^{2−} and one terminal water, whereas Pr2 and Pr4 have tricapped trigonal-prism geometry, finished by nine BDC^{2−}. The Pr–O bond lengths vary from 2.303 to 2.732 Å, comparable with other Pr-containing complexes [13]. The carboxyl groups of BDC^{2−} are bidentate, $\mu_2:\eta^2:\eta^1$ and $\mu_3:\eta^2:\eta^1$ coordinated.

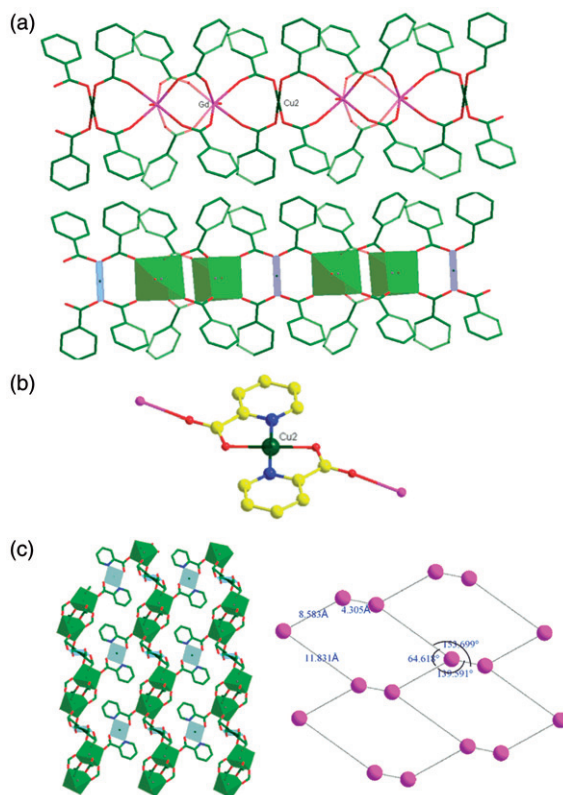


Figure 2. (a) The wires-and-sticks/polyhedral description of the infinite CuGd₂(CO₂)₈ rod-shaped heterometallic carboxylate substructure. (b) the Cu(pic)₂ fragment. (c) the polyhedral description of the Cu–Gd heterometallic honeycomb and the schematic description of the (6, 3) nets.

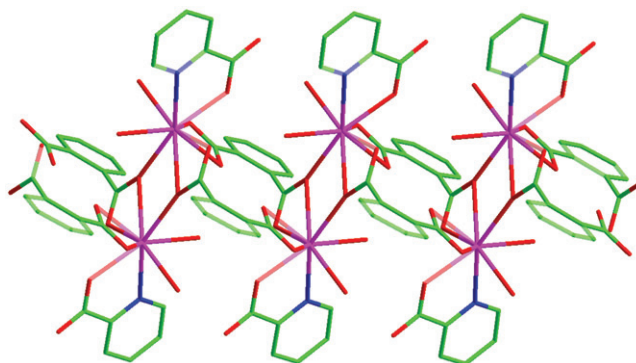


Figure 3. The wire-and-stick description of the 1-D tape structure.

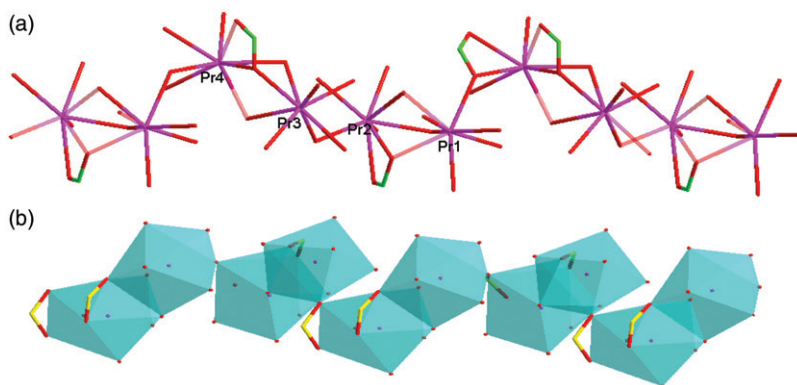


Figure 4. (a) View of the inorganic Pr–O rod in $-\text{Pr}_4\text{--O--Pr}_3\text{--O--Pr}_2\text{--O--Pr}_1-$. (b) polyhedral description of the inorganic Pr–O rod.

Along b , the Pr(III) ions are bridged by $\mu_2\text{-O}$ to construct the inorganic Pr–O rod in the $-\text{Pr}_4\text{--O--Pr}_3\text{--O--Pr}_2\text{--O--Pr}_1-$ arrangement (figure 4), where the Pr–Pr distance is 3.933 Å for Pr4–Pr3, 4.266 Å for Pr3–Pr2, 3.911 Å for Pr2–Pr1, and 4.331 Å for Pr1–Pr4. Furthermore, these Pr–O rods are bridged by BDC^{2-} to construct the 2-D (6, 3)-like network (figure 5); no important supramolecular interactions between layers (separated by ca 11 Å) exist.

3.3. TG and XRD research

The phase purity of **1–3** is confirmed by XRD (Supplementary material; figures S1–S3). The thermal stability of **1–3** has been studied by TG from 30°C to 700°C. Compound **1** is thermally stable to 170°C. Compound **2** lost the free and coordinated water about 70°C–200°C (Exp. 10.4%, Calcd 10.8%). The remaining phase begins to decompose around 360°C. For **3**, the weight loss at 100°C–200°C is ca 1.8%, corresponding to the loss of coordinated water (Calcd 2.1%); the remaining phase is stable to 400°C (figure S4).

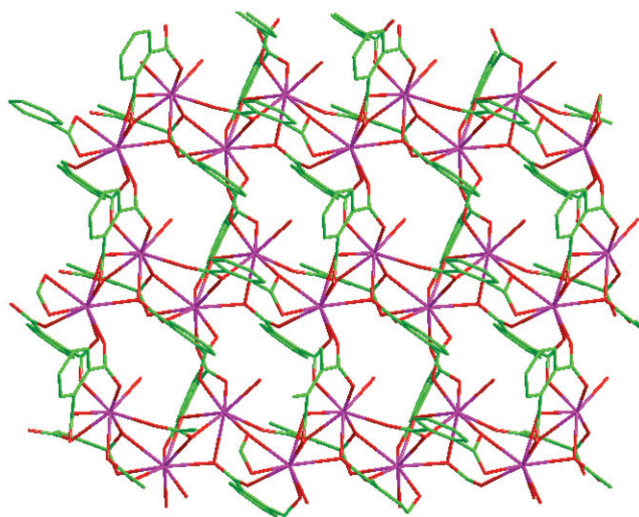


Figure 5. View of the honeycomb-like network.

3.4. Magnetic properties

The $\chi_M T$ of crystal samples of **1–3** has been measured in the temperature range of 2–300 K with applied magnetic fields of 500 Oe. At room temperature, the $\chi_M T$ values of $8.29 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **1**, $7.95 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **2**, and $6.28 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **3** are consistent with the expected values per GdCu ($8.25 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$), Gd ($7.87 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$), and Pr₄ ($6.4 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) as magnetically noninteracting centers ($S_{\text{Gd}} = 7/2$, $S_{\text{Cu}} = 1/2$, $g_{\text{Gd}\cdot\text{Cu}} = 2.0$, $S_{\text{Pr}} = 1$, $L_{\text{Pr}} = 5$, and $g_{\text{Pr}} = 0.8$) [14], respectively. From $\chi_M T$ versus T plots of **1–3**, it is clear that **1** shows somewhat ferromagnetic behavior and **2** and **3** display antiferromagnetic behavior. Fitting $1/\chi_M$ versus T plots at 2–300 K for **1** and **2** and 34–300 K for **3** by the Curie–Weiss law ($\chi_M = C/(T - \theta)$) gives $C = 8.3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **1**, $7.9 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **2**, $7.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **3**, and $\theta = +0.25 \text{ K}$ for **1**, -0.32 K for **2**, -35.4 K for **3**, where the small positive or negative θ values indicate a weak ferromagnetic or antiferromagnetic interaction in **1** and **2** and the big negative θ values suggest strong ferromagnetic interaction in **3** (figures 6–8).

4. Conclusion

In this work, we explored the Cu(II)–4f–Hpic–H₂BDC system, successfully isolating a 3d–4f–pic–PhCOO coordination polymer with honeycomb structure. Further investigation results in the formation of one Gd(III)–pic–BDC compound with the 1-D tape-like configuration and one Pr–BDC compound showing (6, 3) nets. In literature, a large number of reports about 4f or 3d–3f compounds exist [15], but few reports explored product diversity controlled by reaction temperature or different 4f elements. By contrast, in the Cu(II)–4f–Hpic–H₂BDC system control of reaction temperature or 4f element gives one 3d–4f and two 4f compounds, where the formation of **1** and **2** is

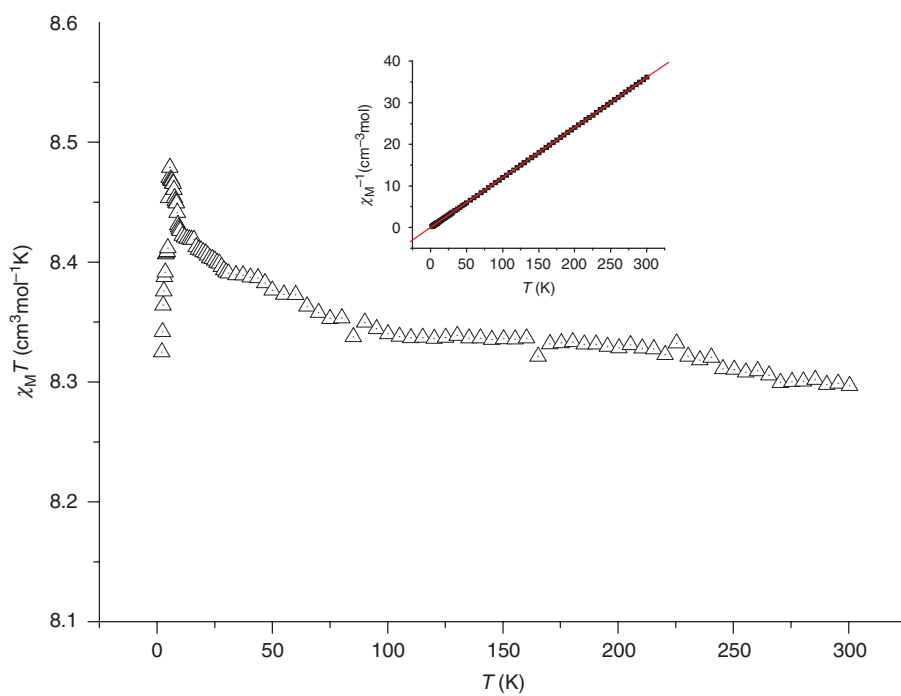


Figure 6. $\chi_M T$ vs. T plot of **1** with the inserted χ_M^{-1} vs. T plot.

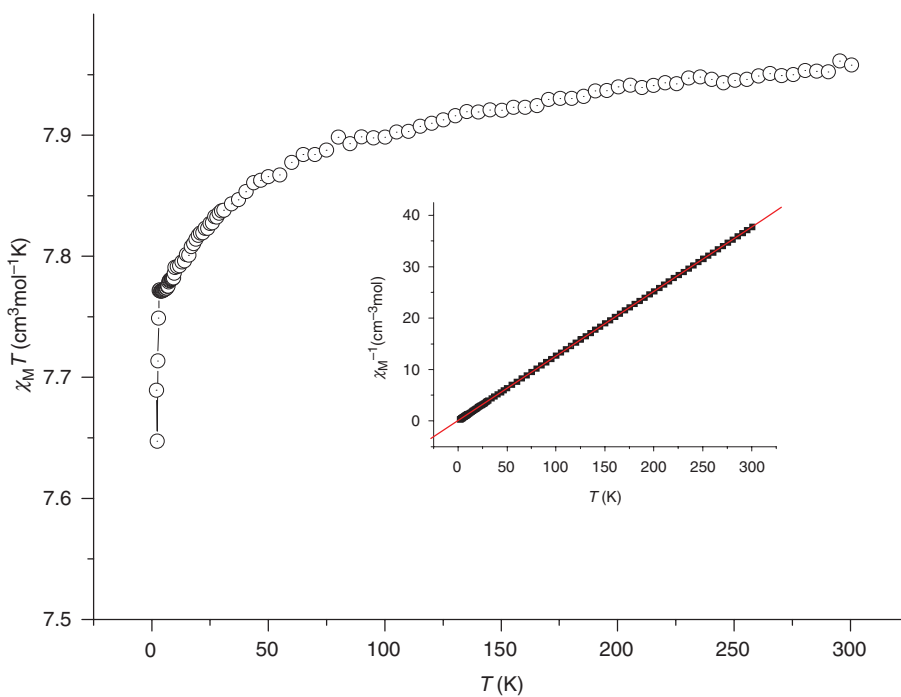


Figure 7. $\chi_M T$ vs. T plot of **2** with the inserted χ_M^{-1} vs. T plot.

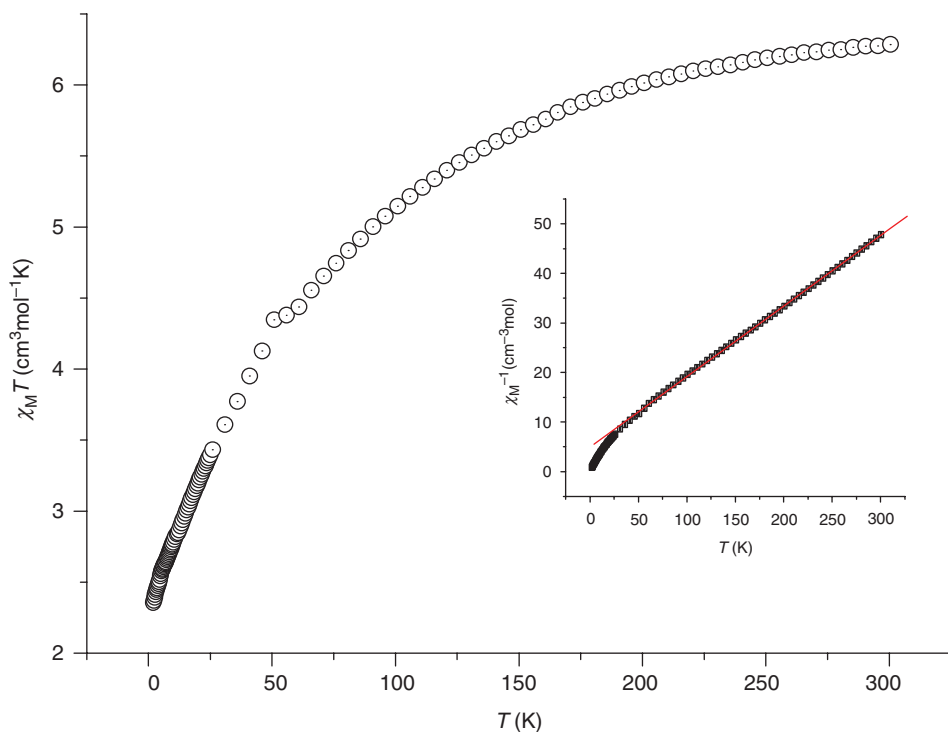


Figure 8. $\chi_M T$ vs. T plot of **3** with the inserted χ_M^{-1} vs. T plot.

controlled by reaction temperature, namely 160°C for **1** and 170°C for **2**, and the yield of **3** is element-dependent, namely Gd for **1–2** and Pr for **3**. Moreover, in contrast to the reports [15], the present case has developed a new dual-ligand approach to target 4f or 3d–4f compounds. To some extent, the present work demonstrates the potential of the Cu(II)–4f–Hpic–H₂BDC system, and we anticipate that if H₂BDC in this Cu(II)–4f–pic–BDC system is replaced by other multicarboxylate ligands, construction of high-dimensional frameworks will be expected; this is our ongoing work.

Supplementary material

CCDC Nos: 641312(**1**), 641313(**2**), and 641314(**3**).

Acknowledgment

This work was supported by the Start-up Foundation of East China Institute of Technology.

References

- [1] (a) H.B. Kagan. *Chem. Rev.*, **102**, 1805 (2002); (b) C.E. Plečnik, S. Liu, S.G. Shore. *Acc. Chem. Res.*, **36**, 499 (2003).
- [2] Y. Matuura, S. Matsushima, M. Sakamoto, Y. Sadaoka. *J. Mater. Chem.*, **3**, 767 (1993).
- [3] M. Sakamoto, K. Matsuki, R. Ohsumi, Y. Nakayama, A. Matsumoto, H. Okawa. *Bull. Chem. Soc. Jpn.*, **65**, 2278 (1992).
- [4] (a) A. Rath, E. Aceves, J. Mitome, J. Liu, U.S. Ozkan, S.G. Shore. *J. Mol. Catal. A: Chem.*, **165**, 103 (2001); (b) S.G. Shore, E.R. Ding, C. Park, M.A. Keane. *Catal. Commun.*, **3**, 77 (2002).
- [5] (a) C.E. Plečnik, S. Liu, S.G. Shore. *Acc. Chem. Res.*, **36**, 499 (2003); (b) S. Liu, E.A. Meyers, S.G. Shore. *Angew. Chem. Int. Ed.*, **41**, 3609 (2002); (c) Y.P. Ren, L.S. Long, B.W. Mao, Y.Z. Yuan, R.B. Huang, L.S. Zheng. *Angew. Chem. Int. Ed.*, **42**, 532 (2003); (d) G.B. Deacon, C.M. Forsyth, T. Behrsing, K. Konstas, M. Forsyth. *Chem. Commun.*, 2820 (2002).
- [6] (a) M.B. Zhang, J. Zhang, S.T. Zheng, G.Y. Yang. *Angew. Chem. Int. Ed.*, **44**, 1385 (2005); (b) J.W. Cheng, J. Zhang, S.T. Zheng, M.B. Zhang, G.Y. Yang. *Angew. Chem. Int. Ed.*, **45**, 75 (2006); (c) X.J. Gu, D.F. Xue. *Inorg. Chem.*, **45**, 9257 (2006); (d) S.-I. Noro, H. Miyasaka, S. Kitagawa, T. Wada, T. Okubo, M. Yamashita, T. Mitani. *Inorg. Chem.*, **44**, 133 (2005).
- [7] F.E. Jacobsen, J.A. Lewis, S.M. Cohen. *J. Am. Chem. Soc.*, **128**, 3156 (2006).
- [8] (a) D. Bayot, M. Degand, B. Tinant, M. Devillers. *Inorg. Chim. Acta*, **359**, 1390 (2006); (b) P. Starynowicz. *Acta Crystallogr., Sect. C*, **49**, 1895 (1993); (c) A.Q. Wu, G.H. Guo, C. Yang, F.K. Zheng, X. Liu, G.C. Guo, J.S. Huang, Z.C. Dong, Y. Takano. *Eur. J. Inorg. Chem.*, 1947 (2005).
- [9] (a) F. Luo, Y.X. Che, J.M. Zheng. *Cryst. Growth Des.*, **6**, 2432 (2006); (b) F. Luo, S.R. Batten, Y.X. Che, J.M. Zheng. *Chem. Eur. J.*, **13**, 4948 (2007); (c) F. Luo, Y.X. Che, J.M. Zheng. *CrystEngComm.*, **10**, 1613 (2008).
- [10] X.M. Zhang. *Coord. Chem. Rev.*, **249**, 1201 (2005).
- [11] N.E. Brese, M. O'Keeffe. *Acta Crystallogr.*, **B47**, 192 (1991).
- [12] B. Li, W. Gu, L.-Z. Zhang, J. Qu, Z.-P. Ma, X. Liu, D.-Z. Liao. *Inorg. Chem.*, **45**, 10425 (2006).
- [13] (a) A. Bencini, C. Benelli, A. Caneschi, R.L. Barlin, A. Dei, D. Gatteschi. *J. Am. Chem. Soc.*, **107**, 8128 (1985); (b) Q.-D. Liu, S. Gao, J.-R. Li, B.-Q. Ma, Q.-Z. Zhou, K.-B. Yu. *Polyhedron*, **21**, 1097 (2002).
- [14] O. Kahn. *Molecular Magnetism*, Wiley-VCH, New York, (1993).
- [15] (a) X.S. Wu, Y.B. Zhang, X. Li, P.Z. Li. *J. Coord. Chem.*, **62**, 797 (2009); (b) F. Chen, W.M. Lu, Y. Zhu, B. Wu, X.M. Zheng. *J. Coord. Chem.*, **62**, 808 (2009); (c) Z.Q. Ming, Y.X. Miao, S.F. Si. *J. Coord. Chem.*, **62**, 833 (2009); (d) M.L. Zhang, F.G. Xin, Z.L. Wang. *J. Coord. Chem.*, **62**, 2347 (2009).