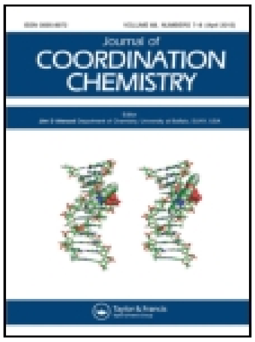


Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

Ionothermal synthesis, thermal behavior, and fluorescence of two gallium-1,4-benzenedicarboxylate-based MOFs

Sa-Ying Li & Zhi-Hong Liu

To cite this article: Sa-Ying Li & Zhi-Hong Liu (2015) Ionothermal synthesis, thermal behavior, and fluorescence of two gallium-1,4-benzenedicarboxylate-based MOFs, Journal of Coordination Chemistry, 68:10, 1765-1775, DOI: 10.1080/00958972.2015.1025769

To link to this article: http://dx.doi.org/10.1080/00958972.2015.1025769

Accepted author version posted online: 04 Mar 2015.
Published online: 27 Mar 2015.

Submit your article to this journal

Article views: 63

View related articles

View Crossmark data

Full Terms & Conditions of access and use can be found at
http://www.tandfonline.com/action/journalInformation?journalCode=gcoo20

Download by: [Mizoram University] **Date:** 28 December 2015, At: 14:33

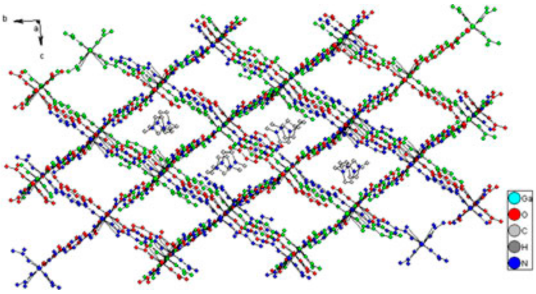
Journal of Coordination Chemistry, 2015
Vol. 68, No. 10, 1765–1775, http://dx.doi.org/10.1080/00958972.2015.1025769

Ionothermal synthesis, thermal behavior, and fluorescence of two gallium-1,4-benzenedicarboxylate-based MOFs

SA-YING LI†‡ and ZHI-HONG LIU†*

†Key Laboratory for Macromolecular Science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, PR China
‡Department of Chemistry and Chemical Engineering, Shaanxi Xueqian Normal University, Xi'an, PR China

(*Received 14 June 2014; accepted 23 February 2015*)



Two gallium-1,4-benzenedicarboxylate-based MOFs, $[C_6H_{11}N_2][Ga(BDC)_2]$ (**1**) and $[C_7H_{13}N_2][Ga(BDC)_2]$ (**2**), were synthesized under ionothermal conditions. Their structures are characterized as a 3-D framework with larger rings constructed by the GaO_4 polyhedra and BDC^{2-} linkers, in which three sets of frameworks are interpenetrated to form a three-fold interpenetration.

Two gallium-based 3-D metal–organic frameworks, $[C_6H_{11}N_2][Ga(BDC)_2]$ (**1**) and $[C_7H_{13}N_2][Ga(BDC)_2]$ (**2**) (BDC = 1,4-benzenedicarboxylate), have been synthesized under ionothermal conditions and characterized by elemental analysis, FT-IR, XRD, and TG. Single-crystal X-ray diffraction studies reveal that **1** and **2** are isostructural. Both complexes crystallize in the monoclinic system with space group $P2_1/c$. Their structures are characterized as a 3-D framework with larger rings constructed by GaO_4 polyhedra and BDC^{2-} linkers, in which three sets of frameworks are interpenetrated along the *a* axis. The used IL cation is located in the pore and compensates for the negative charge of the framework. Thermal behavior and fluorescence of **1** have been studied.

Keywords: Gallium complexes; Ionothermal synthesis; Crystal structure; Thermal behavior; Fluorescence property

---

*Corresponding author. Email: liuzh@snnu.edu.cn

© 2015 Taylor & Francis

Downloaded by [Mizoram University] at 14:33 28 December 2015

Downloaded by [Mizoram University] at 14:33 28 December 2015

1. Introduction

The synthesis of porous metal–organic frameworks (MOFs) has been an area of rapid growth. Many new such compounds have been synthesized and studied for their potential applications in luminescence, catalysis, gas adsorption, and separation [1, 2]. Efforts have been devoted to exploration of MOFs with different functionalities and to development of new synthetic methods. Besides traditional hydro/solvothermal synthesis methods, ionothermal synthesis, that is using ionic liquid (IL) as solvent, has been shown to be a highly promising synthetic route for a variety of MOFs [3]. In recent years, this method has received attention because of the outstanding properties of the ILs: nonflammability, negligible vapor pressure, high polarity, etc. Usually, ILs behave as solvents, structure-directional template, or charge-compensating groups in the reaction systems, thus the influences of both the cationic and anionic parts of ILs on the MOF structures have been studied. Frequently, the cationic parts are structural templates being located in the cavities of skeleton frameworks [4].

The MOF system formed by divalent transition metals and organic aromatic carboxylic acid ligands, which usually exhibit strong coordination ability and flexible coordination mode, has been widely investigated. Compared with the well-developed divalent transition MOFs, group 13 coordination polymers based on aromatic carboxylic acid ligands are relatively rare.

Ga(III) attracts attention because it has flexible coordination geometries, as exemplified by tetrahedral GaO_4, trigonal bipyramidal GaO_5, and octahedral GaO_6. Several gallium–carboxylate organic framework crystalline materials with unusual structures and useful properties have been synthesized [5–7]. 1,4-Benzenedicarboxylate (BDC^{2-}) is a good multidentate aromatic carboxylate ligand. Several gallium-1,4-benzenedicarboxylate organic framework crystalline materials have been synthesized, such as $Ga(OH)(O_2C\text{-}C_6H_4\text{-}CO_2]\cdot H_2O$ (MIL-53) [8], $GaOH(C_8O_4H_4)\cdot 0.9DMF\cdot zH_2O$(MIL-68) [9], $Ga(OH)(BDC)\cdot 0.74H_2BDC$ [10], Ga(OH,F)(BDC)$\cdot 0.74H_2BDC$ [10], Ga(OH,F)(BDC)$\cdot C_5H_5N$ [10], and $Ga(OH_{0.9}F_{0.1})(BDC)\cdot 0.9H_2O$ [11]. However, the synthesis of these gallium-based MOFs has been limited to hydro/solvothermal method. In these gallium-based MOFs, the Ga(III) ions are all six-coordinate and the solvent molecules are all located in the tunnels. For example, in MIL-53(Ga), the water species are trapped within the channels; in the MIL-68 (Ga), DMF moieties are located in the triangular tunnels; and in the $Ga(OH)(BDC)\cdot 0.74H_2BDC$ and Ga(OH,F)(BDC)$\cdot C_5H_5N$, free H_2BDC molecules and C_5H_5N are inside the channels, respectively. Considering the cationic parts in ILs might act as structural templates and charge-compensating groups located in the cavities of skeleton frameworks, we thought that the MOFs might be obtained using the ionothermal synthesis method.

In this work, we present the ionothermal synthesis, crystal structure, and thermal behaviors of two gallium-1,4-benzenedicarboxylate-based MOFs, $[C_6H_{11}N_2][Ga(BDC)_2]$ (**1**) and $[C_7H_{13}N_2][Ga(BDC)_2]$ (**2**). To the best of our knowledge, this is the first example of 3-D gallium-based frameworks with a three-fold interpenetration mode.

2. Experimental

2.1. *Synthesis and characterization*

All the chemical reagents used in our experiments were of analytical grade and used without purification. Single crystals of **1** and **2** were obtained from a mixture of Ga_2O_3,

Downloaded by [Mizoram University] at 14:33 28 December 2015

$Co(CH_3COO)_2{\cdot}4H_2O$, H_3BO_3, H_2BDC, and $C_6H_{11}N_2Br$ (1-ethyl-3-methylimidazolium bromide)/$C_7H_{13}N_2Br$ (1-propyl-3-methylimidazolium bromide) in the molar ratio of 1 : 1 : 8 : 1 : 14 for **1** and **2**, respectively. The final mixture was stirred for several hours at room temperature and then crystallized in a Teflon-lined autoclave at 180 °C for 7 days. After it slowly cooled to room temperature, the colorless single crystals were recovered by filtration, washed with deionized water and ethanol, respectively, and dried in air at ambient temperature. Anal. Calcd for **1**: C, 51.90; H, 3.76; N, 5.50%. Found: C, 51.62; H, 3.78; N, 5.41%. For **2**: C, 52.81; H, 4.05; N, 5.36%. Found: C, 52.43; H, 3.98; N, 5.41%.

The obtained samples were characterized by elemental analysis (determined on a Vario EL III Elemental Analyzer), FT-IR spectroscopy (recorded from 400 to 4000 cm^{-1} on a Nicolet NEXUS 670 spectrometer with KBr pellets at room temperature), and thermogravimetric analysis (TGA) (performed on a SDT Q600 thermal analyzer under N_2 with a heating rate of 10 °C min^{-1}). The morphology of the sample was investigated by scanning electron microscopy (SEM, Philips-FEI, Quanta200). Fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer at room temperature. UV–vis absorption spectra were recorded on a UV–vis-NIR Spectrophotometer (Lambd 950).

2.2. *Determination of crystal structures*

Crystals of **1** (dimensions 0.22 × 0.18 × 0.17 mm^3) and **2** (dimensions 0.22 × 0.20 × 0.17 mm^3) were carefully selected under an optical microscope and data collections were performed on a CCD automatic diffractometer (CrysAlisPro, Oxford Diffraction Ltd, Version 1.171.34.36) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using the ω-scan mode at room temperature. An empirical absorption correction was applied using the semi-empirical from equivalents program [12]. The structures were solved by

Table 1. Crystal data and structure refinement for **1** and **2**.

Compounds	1	2
Empirical formula	$C_{22}H_{19}GaN_2O_8$	$C_{23}H_{21}GaN_2O_8$
Formula weight	509.11	523.14
Temperature (K)	293(2)	293(2)
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a (Å)	a = 6.8573(5)	a = 6.7957(4)
b (Å)	b = 31.1640(19)	b = 31.230(2)
c (Å)	c = 11.1749(11)	c = 11.3264(6)
β (°)	β = 105.515(8)	β = 105.087(6)
Volume (Å^3)	2301.1(3)	2320.9(2)
Z, Calculated density (g cm^{-3})	4, 1.470	4, 1.497
Absorption coefficient (mm^{-1})	1.245	1.237
$F(0\,0\,0)$	1040	1072
Crystal size (mm)	0.19 × 0.18 × 0.15	0.20 × 0.17 × 0.15
Theta range for data collection (°)	3.08–26.00	3.17–24.67
Limiting indices	$-8 \le h \le 8$, $-36 \le k \le 38$, $-13 \le l \le 10$	$-7 \le h \le 7$, $-33 \le k \le 24$, $-13 \le l \le 10$
Reflections collected	9777 / 4512	6931 / 2996
Data / restraints / parameters	4512 / 8 / 300	2996 / 0 / 309
Goodness-of-fit on F^2	1.065	1.037
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0522$, $wR_2 = 0.1289$	$R_1 = 0.0396$, $wR_2 = 0.0920$
R indices (all data)	$R_1 = 0.0668$, $wR_2 = 0.1387$	$R_1 = 0.0501$, $wR_2 = 0.0960$
Largest diff. peak and hole (e Å^{-3})	0.926 and −0.688	0.387 and −0.270

Downloaded by [Mizoram University] at 14:33 28 December 2015

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2***.

$[C_6H_{11}N_2][Ga(BDC)_2]$ (**1**)			
Ga(1)–O(1)	1.847(3)	O(4)–Ga(1)–O(7)	96.58(13)
Ga(1)–O(4)	1.838(3)	O(1)–Ga(1)–O(7)	109.85(14)
Ga(1)–O(6)	1.850(3)	O(6)–Ga(1)–O(7)	127.17(14)
Ga(1)–O(7)	1.853(3)		
O(4)–Ga(1)–O(1)	121.38(14)		
O(4)–Ga(1)–O(6)	106.44(14)		
O(1)–Ga(1)–O(6)	97.61(13)		
$[C_7H_{13}N_2][Ga(BDC)_2]$ (**2**)			
Ga(1)–O(1)	1.849(2)	O(6)–Ga(1)–O(8)#3	97.68(12)
Ga(1)–O(6)	1.848(3)	O(1)–Ga(1)–O(8)#3	107.86(12)
Ga(1)–O(4)	1.854(3)	O(4)–Ga(1)–O(8)#3	126.49(12)
Ga(1)–O(8)#3	1.857(3)		
O(6)–Ga(1)–O(1)	122.52(12)		
O(6)–Ga(1)–O(4)	106.51(12)		
O(1)–Ga(1)–O(4)	98.12(12)		

*Symmetry transformations used to generate equivalent atoms: (#3) $x-1$, $-y+3/2$, $z-1/2$.

direct methods using SHELXS-97 [13]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogens were located at geometrically calculated positions and refined with isotropic thermal parameters. Crystallographic data for **1** and **2** are presented in table 1. The main bond lengths and angles are listed in table 2. CCDC 938723 and 966478 contain the supplementary crystallographic data for this article.

3. Results and discussion

3.1. *FT-IR spectra*

As shown in figure 1, the IR spectrum of **1** is very similar to that of **2** from 400–2000 cm^{-1}, indicating their similar structures. The peaks at 1579 and 1360 cm^{-1} correspond to

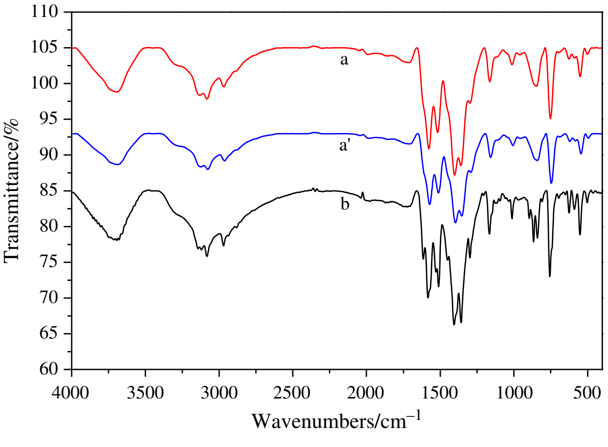


Figure 1. FT-IR spectra of **1** (a, a′) and **2** (b), here a′ is the sample which was crystallized from acetone solution after the solvent was volatilized.

asymmetric and symmetric vibrations of the carboxylate group (COO^-), and the difference in the value between them is more than 200 cm^{-1}, which indicates that the carboxylates are monodentate ligands [14]. The bands at 1163 and 550 cm^{-1} are attributed to the Ga–O stretch.

3.2. *Description of crystal structures*

Single-crystal X-ray diffraction revealed that **1** and **2** are isostructural, and here $[C_6H_{11}N_2]$ $[Ga(BDC)_2]$ (**1**) will be described. In **1**, the asymmetric unit consists of one gallium ion, two BDC^{2-} ligands, and one $[C_6H_{11}N_2]^+$ cation, as shown in figure 2. Ga(III) is four-coordinate with four carboxyl oxygens (O1, O4, O6, and O7) from four different BDC^{2-} ligands in monodentate coordination modes, forming a distorted tetrahedron (GaO_4). The Ga–O bond lengths are 1.838(3) – 1.853(3) Å and the O–Ga–O bond angles change from 96.58(13)° to 127.17(14)°, which are in good agreement with those of a previously reported Ga(III) complex, $Ga_6(1,3,5\text{-}BTC)_8 \cdot 6DMA \cdot 3DMF \cdot 26H_2O$, that was four-coordinate with four carboxyl oxygen donors [7]. In this complex the bond lengths of Ga–O are 1.832 Å and the O–Ga–O bond angles change from 103.99(4)° to 121.09(8)°.

In the crystal, each BDC^{2-} is μ-2 BDC^{2-}, in which both carboxyls are monodentate to Ga(III). Each μ-2 BDC^{2-} is a μ_2-bridge to link two Ga(III) ions, forming a 3-D anionic framework along the *a* axis, as shown in figure 3. The IL cations $[C_6H_{11}N_2]^+$ are located in the 3-D framework and compensate for the negative charges of the whole framework.

Downloaded by [Mizoram University] at 14:33 28 December 2015

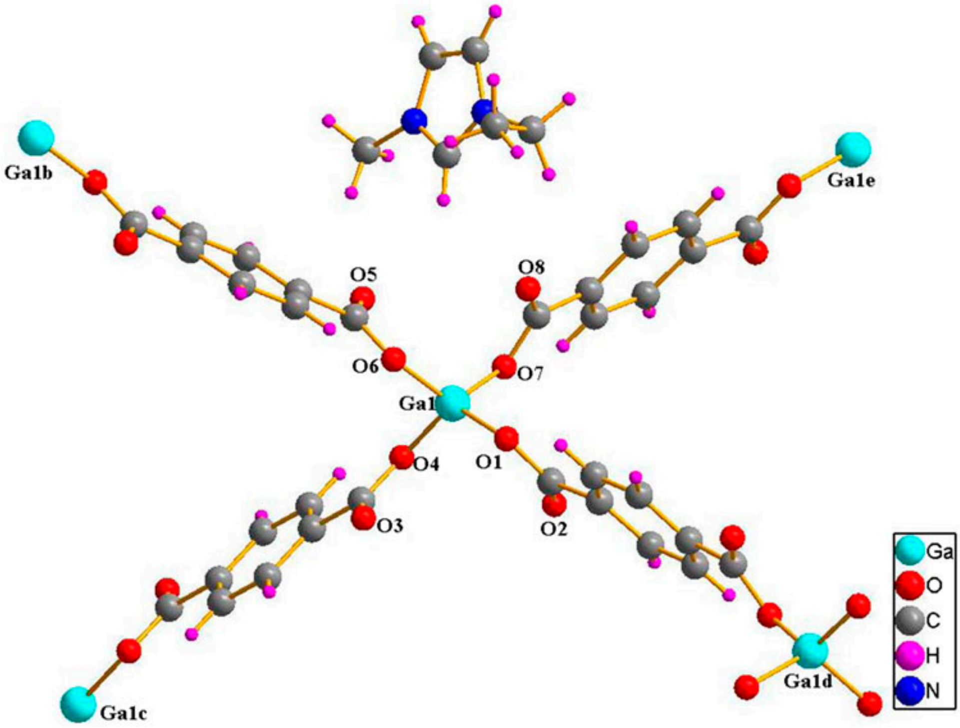


Figure 2. Coordination environments of Ga(III) and the BDC^{2-} ligand in **1**. The probability ellipsoid is 30%.

Downloaded by [Mizoram University] at 14:33 28 December 2015

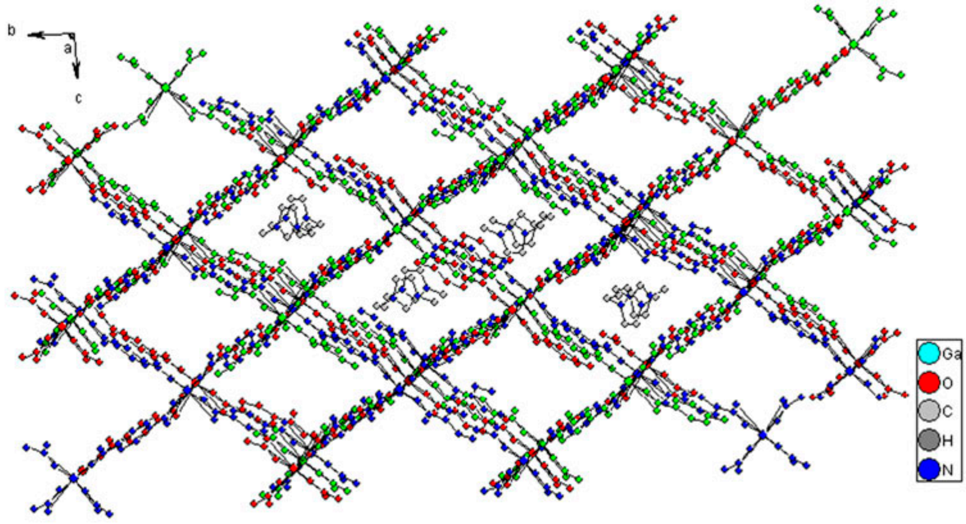


Figure 3. Packing view along the *a* axis of **1**.

The pore size of **1** is 18.85 × 14.59 Å given as the cross-pore Ga–Ga distances. According to Platon calculation, the solvent-accessible void of the crystal accounts for 1.5% of the crystal volume. As a comparison, the pore sizes are 17.53 × 13.66 Å for Ga(OH)(BDC)·0.74H_2BDC [10], 17.41 × 12.16 Å for Ga(OH,F)(BDC)·0.74H_2BDC [10], and 17.29 × 12.91 Å for Ga(OH,F)(BDC)·C_5H_5N [10]. It is obvious that the pore size of **1** is slightly bigger than that in these compounds.

From the topological view, each Ga can be simplified as a four-connected node with BDC as linkers. Thus, the 3-D framework of **1** is a familiar four-connected *dia*-topology. It should be pointed out that three sets of the frameworks are interpenetrated along the *a* axis to form a three-fold interpenetration, as shown in figure 4.

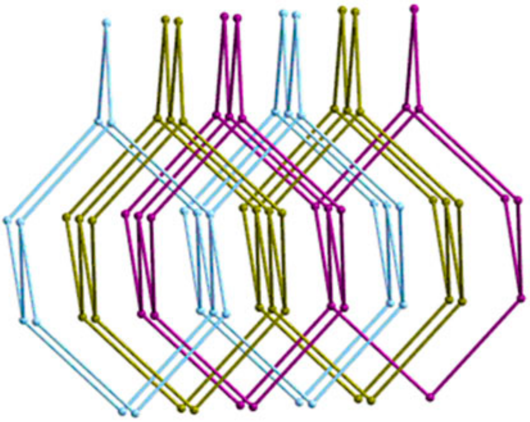


Figure 4. Topological graph representation of the 3-D structure of **1**.

Downloaded by [Mizoram University] at 14:33 28 December 2015

3.3. *X-ray powder diffraction pattern*

As shown in figures 5 and 6, the diffraction peaks on powder X-ray diffraction patterns correspond well in position with those of the simulated patterns on the basis of single-crystal structure of **1** and **2**, respectively, which indicates that the synthesized samples phase are pure.

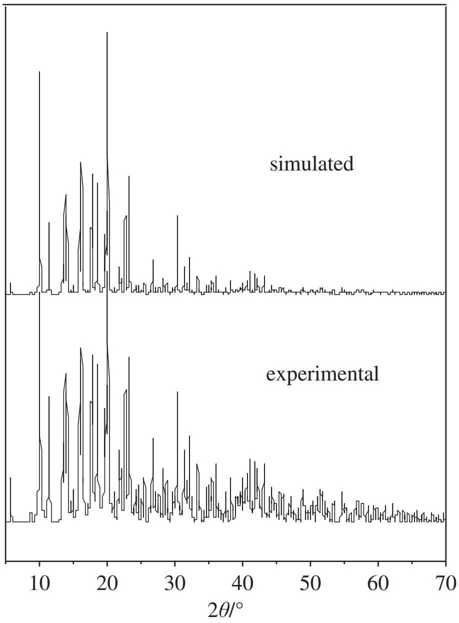


Figure 5. X-ray powder diffraction pattern of **1**.

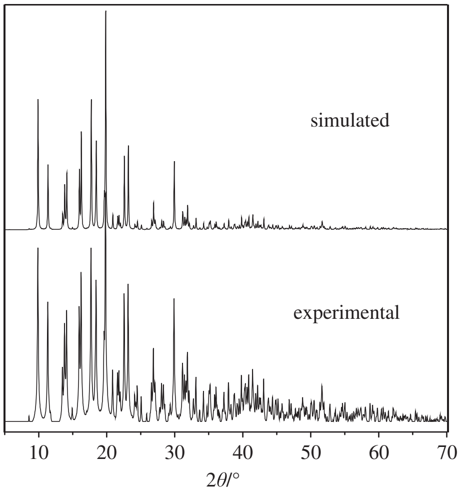


Figure 6. X-ray powder diffraction pattern of **2**.

3.4. *Thermal behaviors*

As shown in figure 7, the thermogravimetric (TG) curves show similar weight loss behavior for both compounds, which also indicate their similar structures. The two compounds were stable below 350 °C for **1** and 400 °C for **2**. After that temperature, they began to decompose in two steps and have total weight losses of 79.13 and 79.64%, respectively. The first weight losses of 54.53% for **1** and 55.80% for **2** correspond to removal of one BDC and the ILs cation from 350 to 450 °C for **1** and from 400 to 495 °C for **2**, which were compared with the calculated values of 54.11% for **1** and 55.30% for **2**, respectively. The second weight losses correspond to removal of the other organic matter. The final residue was Ga_2O_3 phase, which was confirmed by the PXRD pattern (figure 8) of the residue of **1**.

3.5. *Fluorescence property*

As shown in figure 9, upon excitation of the solid sample at 312 nm, **1** exhibits a fluorescent emission at 395 nm. The emission band was observed at 388 nm for free H_2BDC

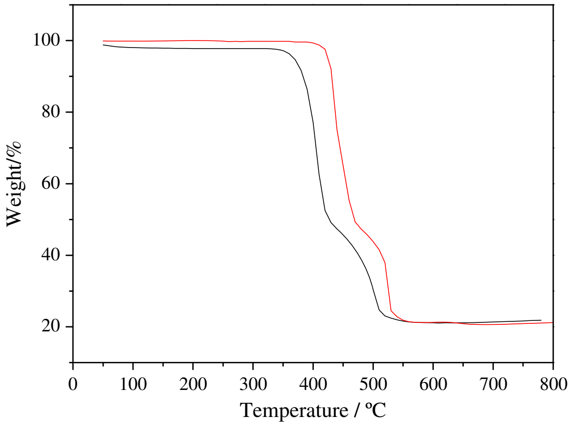


Figure 7. TG curves of **1** and **2**.

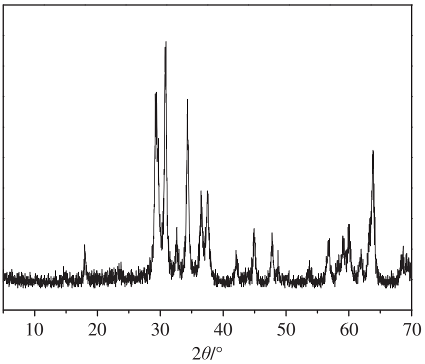


Figure 8. X-ray powder diffraction pattern of the residue for **1**.

Downloaded by [Mizoram University] at 14:33 28 December 2015

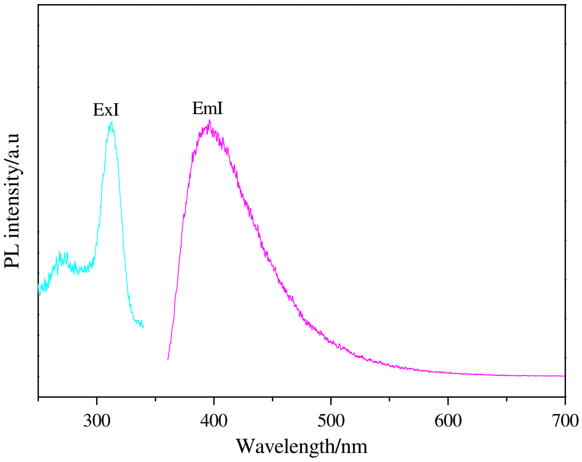


Figure 9. Solid-state excitation and emission spectra of **1** at room temperature.

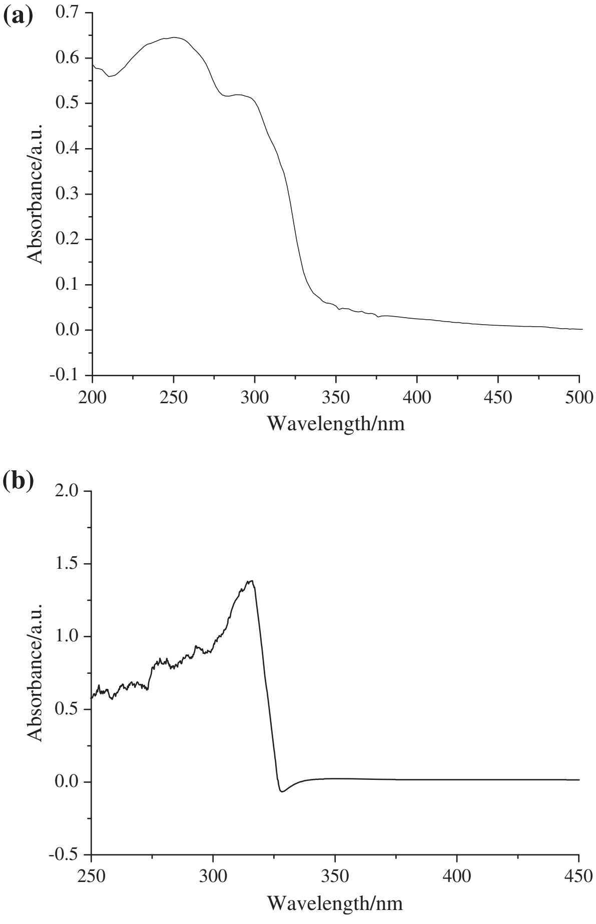


Figure 10. (a) The solid-state UV–vis absorption spectrum of **1**; (b) The absorption spectrum of **1** in acetone.

Downloaded by [Mizoram University] at 14:33 28 December 2015

Downloaded by [Mizoram University] at 14:33 28 December 2015

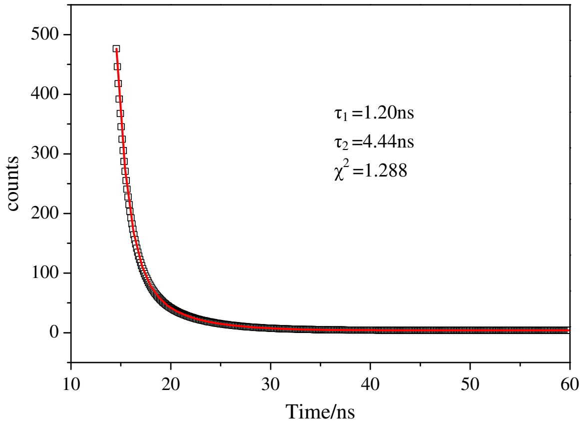


Figure 11. The fitted decay curve monitored at 395 nm for **1** in the solid state at room temperature. The sample was excited at 312 nm. Blank circles: experimental data; Solid line: fitted by Fit = A + B1 × exp($-t/\tau_1$) + B2 × exp($-t/\tau_2$).

ligand with excitation at 270 nm [15]. The emission peak of **1** is similar to that of H_2BDC. Therefore, the emission band of **1** could be assigned to ligand-centered electronic transitions; the difference in their emissions is probably due to the differences in metal ions and coordination environment around them [16].

The absorption spectrum of **1** was measured using powdered crystal, as shown in figure 10(a), in which there exist two absorption bands at 252 nm and 290 nm. Upon excitation of the solid sample at 252 nm or 290 nm, **1** exhibits a fluorescent emission at 395 nm. But when the 395 nm was chosen to measure the excitation spectrum of **1**, it was 312 nm. So, the absorption spectrum of **1** in acetone was also measured. As shown in figure 10(b), there exists a strong absorption band at 312 nm, which is consistent with the excitation band in fluorescence spectrum of **1** in solid state. In order to confirm that **1** maintains its integrity upon dissolution, we have done the IR spectrum of the solid sample (a′*)* which was crystallized from acetone solution after the solvent was volatilized. It can be seen from figure 1 that the IR spectrum of sample a′ is in agreement with that of sample *a* for **1**.

The emission decay lifetime of **1** was also measured and the curve (figure 11) is best fitted by biexponentials in the solid state. The emission decay lifetimes of **1** are $\tau_1 = 1.20$ ns, $\tau_2 = 4.44$ ns, $\chi^2 = 1.288$. The nanosecond range of lifetime in the solid state at room temperature indicates that the emission is fluorescent [17].

4. Conclusion

We have synthesized two new 3-D framework gallium complexes, $[C_6H_{11}N_2][Ga(BDC)_2]$ (**1**) and $[C_7H_{13}N_2][Ga(BDC)_2]$ (**2**), under ionothermal conditions, which presents the first example of IL not only as the reaction medium but also as the reactant in this system. **1** and **2** have a three-fold interpenetration structure with larger rings constructed by the GaO_4 polyhedra and the BDC^{2-} linkers.

Supplementary material

CCDC 938723 and 966478 contain the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk [or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by Innovation Funds of Graduate Programs, SNNU [grant number 2013CXB022] and National Natural Science Foundation of China [grant number 21173143].

Downloaded by [Mizoram University] at 14:33 28 December 2015

References

[1] C. Janiak. *Dalton Trans.*, **32**, 2781 (2003).
[2] L.Q. Ma, C. Abney, W.B. Lin. *Chem. Soc. Rev.*, **38**, 1248 (2009).
[3] (a) E.R. Parnham, R.E. Morris. *Acc. Chem. Res.*, **40**, 1005 (2007); (b) R.E. Morris. *Chem. Commun.*, **21**, 2990 (2009); (c) J.R. Li, Z.L. Xie, X.W. He, L.H. Li, X.Y. Huang. *Angew. Chem. Int. Ed.*, **50**, 11395 (2011).
[4] L. Xu, Y.U. Kwon, B. de Castro, L. Cunha-Silva. *Cryst. Growth Des.*, **13**, 1260 (2013).
[5] P. O'Brien, H. Salacinski, M. Motevalli. *J. Am. Chem. Soc.*, **119**, 12695 (1997).
[6] G.P. Zhou, Y.L. Yang, R.Q. Fan. *Inorg. Chem. Commun.*, **16**, 17 (2012).
[7] D. Banerjee, S. Jin Kim, H. Wu, W. Xu, L.A. Borkowski, J. Li, J.B. Parise. *Inorg. Chem.*, **50**, 208 (2011).
[8] C. Volkringer, T. Loiseau, N. Guillou, G. Ferey, E. Elkaımc, A. Vimont. *Dalton Trans.*, **12**, 2241, (2009).
[9] C. Volkringer, M. Meddouri, T. Loiseau, N. Guillou, J. Marrot, G. Férey, M. Haouas, F. Taulelle, N. Audebrand, M. Latroche. *Inorg. Chem.*, **47**, 11892 (2008).
[10] M. Vougo-Zanda, J. Huang, E. Anokhina, X. Wang, A.J. Jacobson. *Inorg. Chem.*, **47**, 11535 (2008).
[11] A. Boutin, D. Bousquet. *J. Phys. Chem. C*, **117**, 8180 (2013).
[12] G.M. Sheldrick. *A Program for the Siemens Area Detector Absorption Correction*, University of Göttingen, Germany (1997).
[13] G.M. Sheldrick. *SHELXS 97 Program for Solution of Crystal Structures*, University of Göttingen, Germany (1997).
[14] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn, Wiley, New York, NY (1986).
[15] T. Lee, Z.X. Liu, H.L. Lee. *Cryst. Growth Des.*, **11**, 4146 (2011).
[16] Q.R. Fang, G.S. Zhu, M. Xue, J.Y. Sun, F.X. Sun, S.L. Qiu. *Inorg. Chem.*, **45**, 3582 (2006).
[17] B. Xu, J. Xie, H.M. Hu, X.L. Yang, F.X. Dong, M.L. Yang, G.L. Xue. *Cryst. Growth Des.*, **14**, 1629 (2014).