

# 3-D indium(III)-btc channel frameworks and their ion-exchange properties (btc = 1,3,5-benzenetricarboxylate)

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Received 3 November 2005; received in revised form 27 December 2005; accepted 2 January 2006  
Available online 3 February 2006

## Abstract

Assembly of  $\text{InCl}_3$  with 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{btc}$ ) and pyridine or pyridine derivatives under hydrothermal conditions produces a series of isostructural coordination polymers with the interesting frameworks:  $\{(\text{HL})[\text{In}_4(\text{OH})_4(\text{btc})_3] \cdot \text{L} \cdot 3\text{H}_2\text{O}\}_n$ ,  $\text{L} = \text{pyridine}$  (**1**);  $\text{L} = 2\text{-picoline}$  (**2**);  $\text{L} = 4\text{-picoline}$  (**3**) and  $\{(\text{Hdpea})[\text{In}_4(\text{OH})_4(\text{btc})_3] \cdot 3\text{H}_2\text{O}\}_n$  (**4**) ( $\text{dpea} = 1,2\text{-di(4-pyridyl)ethane}$ ). In these four complexes, carboxyl and hydroxyl oxygen atoms bridge indium(III) centers to form octahedral chain-like sinusoidal curves, which are further interlinked by  $\text{btc}^{3-}$  moieties to generate 3-D frameworks with 1-D channels. The protonated guests HL in **1–3** located at the channels can be fully exchanged by  $\text{K}^+$  ion or partially exchanged by  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  ions.

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**Keywords:** Indium(III); Benzenetricarboxylate; Crystal structure; Ion-exchange; Pyridine derivatives

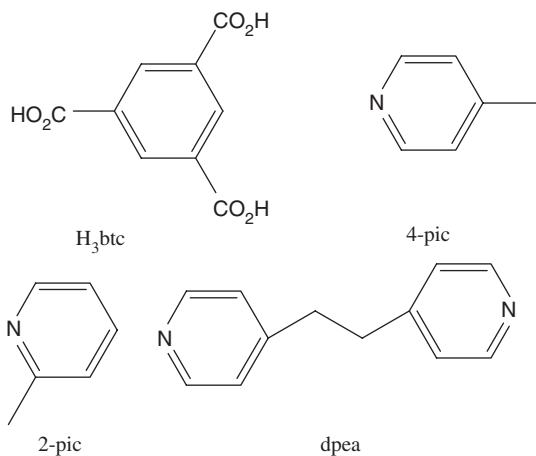
## 1. Introduction

The construction of metal-organic porous hosts represents one of the most challenging subjects due to their potential application in adsorption and separation processes, [1–2] ion-exchange, [3] catalysis [4] and sensor technology [5]. Recently, intense research activities in this field have resulted in enormous number of porous solids with structures and properties different from the well-known zeolite frameworks. In the assembly of metal-organic porous solids, pyridine and its derivatives (pyds) have been employed to deprotonate carboxyl groups in organic ligands, such as 1,3,5-benzenetricarboxylic acids ( $\text{H}_3\text{btc}$ ), (Scheme 1) [6]. Pyridine and pyds can also act as the guests to fill into the cavities of the host frameworks or as the terminal ligands to complete the metal coordination environment [7]. Furthermore, interactions including hydrogen bond contacts and  $\pi-\pi$  stacking are usually found in the pyds-containing system and play an important role

in the assembly process.  $\text{H}_3\text{btc}$  is a promising ligand, providing high symmetry, with diverse charge and multi-connecting ability that has been applied in the design of hybrid complexes. Much current research is being focused on the syntheses and structural characterization of coordination polymers assembled from  $\text{H}_3\text{btc}$  and divalent metal elements [6–8]. The use of trivalent metal elements to date, however, has mostly been confined to the field of rare earth metals compounds, which are typical of high coordination number conformation [9–10] and very similar to the six-, seven- and eight-coordination that are commonly found in the polymers of the IIIA group elements [11,12]. Furthermore, it is postulated that the incorporation of trivalent metal of IIIA group might create diverse structures due to the increased valence charge of metal centers [13]. Based on above idea,  $\text{In}^{\text{III}}$  has been employed and a series of  $\text{In}^{\text{III}}$ -btc complexes with 1-D chain, 2-D layer and 3-D network have been successfully synthesized. Herein, we report four non-interpenetrated 3-D coordination polymers with channels located inside by protonated organic guests:  $\{(\text{HL})[\text{In}_4(\text{OH})_4(\text{btc})_3] \cdot \text{L} \cdot 3\text{H}_2\text{O}\}_n$ ,  $\text{L} = \text{pyridine}$  (**1**);  $\text{L} = 2\text{-picoline}$  (**2**);  $\text{L} =$

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Scheme 1. H<sub>3</sub>btc and pyridine derivatives.

4-picoline (**3**) and  $\{(\text{Hdpea})[\text{In}_4(\text{OH})_4(\text{btc})_3] \cdot 3\text{H}_2\text{O}\}_n$  (**4**) (dpea = 1,2-di(4-pyridyl)ethane).

## 2. Experimental

### 2.1. Materials and physical measurements

All the syntheses were carried out in Teflon-lined stainless-steel autoclaves under autogenous pressure. Chemicals were commercially purchased and used as received. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr pellets. Elemental analyses were carried out on Elementar Vario EL III microanalyzer. Thermal gravimetric (TG) analyses were performed with heating rate of  $15^\circ\text{C min}^{-1}$  on a NETZSCH STA 449C simultaneous TG-DSC instrument. Powder X-ray diffraction (XRD) data were collected on a Rigaku DMAX2500 diffractometer.

### 2.2. Preparations

A mixture of  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$  (147.0 mg, 0.5 mmol), H<sub>3</sub>btc (105 mg, 0.5 mmol), pyridine (typical example: 1.0 mL, 12.2 mmol) and H<sub>2</sub>O (5.0 mL) in 42-mL Teflon-lined stainless-steel vessel was heated at  $165^\circ\text{C}$  for 85 h, and then was cooled to room temperature at a rate of  $6^\circ\text{C h}^{-1}$ , giving light yellow prismatic crystals of **1**. The crystals were collected by density-difference and washed with *N,N*-dimethylformamide (DMF) and water sequentially, giving an isolated yield of 77% based on  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ . Compounds **2**, **3**, and **4** were prepared in similar methods by simply replacing pyridine with 2-picoline (1.0 mL, 10.1 mmol), 4-picoline (1.0 mL, 10.3 mmol) and 1,2-di(4-pyridyl)ethane (1104 mg, 6.0 mmol), respectively, and were obtained in the yields of 42%, 74% and 80%. Elemental analyses and IR spectra (KBr pellet,  $\text{cm}^{-1}$ ) were given: for **1**:  $\text{C}_{37}\text{H}_{30}\text{In}_4\text{N}_2\text{O}_{25}$ , Calcd. (Found) C, 32.63 (32.74); N, 2.06 (2.09); H, 2.22 (2.37). IR: 3419(vs, br), 3254(m),

3086(m, sh), 1626(vs), 1605(sh), 1574(s), 1539(vs), 1491(m), 1449(s), 1372(vs), 1100(w), 1061(w), 935(w), 749(m), 716(m); for **2**:  $\text{C}_{39}\text{H}_{34}\text{In}_4\text{N}_2\text{O}_{25}$ , Anal. Calcd. (Found) C, 33.68 (33.79); N, 2.02 (2.00); H, 2.47 (2.37). IR: 3400(vs, br), 3379(m, br), 3264(m), 3071(m), 2972(m), 1623(s), 1572(m), 1539(s), 1449(s), 1375(vs), 1110(w), 1042(w), 937(w), 769(m), 737(m), 711(m); for **3**:  $\text{C}_{39}\text{H}_{34}\text{In}_4\text{N}_2\text{O}_{25}$ , Anal. Calcd. (Found): C, 33.68 (33.49); N, 2.02 (1.99); H, 2.47 (2.38). IR: 3389(m, br), 3073(m), 2974(m), 2922(m), 1622(vs), 1572(m), 1538(s), 1448(s), 1374(vs), 1110(w), 1048(w,br), 935(w), 809(w), 769(s), 736(m), 710(s); for **4**:  $\text{C}_{39}\text{H}_{32}\text{In}_4\text{N}_2\text{O}_{25}$ , Anal. Calcd. (Found): C, 33.75 (33.46); N, 2.02 (1.95); H, 2.32 (2.17). IR: 3270(s, br), 3074(m), 2971(m), 1623(vs), 1575(s), 1538(vs), 1446(s), 1425(s), 1375(s), 1112(m), 1061(m), 936(m), 846(w), 825(w), 768(s), 737(s), 711(s).

### 2.3. Crystallographic studies

Intensity data were collected on a Rigaku mercury CCD diffractometer with graphite-monochromated  $\text{MoK}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation by using  $\omega - 2\theta$  scan method at room temperature. The structures were solved by direct methods using SHELXS-97 [14] and were refined on  $F^2$  by full-matrix least-squares methods using SHELXL-97 [15]. All non-hydrogen atoms were refined anisotropically except for the Hdpea<sup>+</sup> cation in **4**. All hydrogen atoms were calculated on the ideal positions and refined isotropically. Final  $R = \sum(|F_o| - |F_c|) / \sum|F_o|$ , and  $wR = \{\sum w[(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$  with  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2)/3$ . 2-pic molecules in **2** cannot be located due to the major disordered problem. However, the data were corrected with SQUEEZE [16] for the effects of disordered species so as to improve the  $R$  factor by approximately 2.0%. The crystallographic data are summarized in Table 1.

## 3. Results and discussion

### 3.1. Synthesis

Through the systematic experiments to find out the optimum reaction condition, we believe that the formation of the coordination framework is extremely dependent on the pH value of the reaction system. Pyds are added to adjust the pH value and also act as template guests. So the amount of pyds plays an important role in the resulting structure. The appropriate pH value favoring the generations of **1–4** is ca. 6. With pH value less than 3 the reaction system generates a 2-D layered structure formulated as  $[\text{In}_2(\text{btc})_2(\text{H}_2\text{O})_2]_n \cdot 2n\text{H}_2\text{O}$ , [13] while the reactions would produce the mixture of  $[\text{In}_2(\text{btc})_2(\text{H}_2\text{O})_2]_n \cdot 2n\text{H}_2\text{O}$  and the corresponding compounds of **1–4** when the pH scale ranges from 3 to 4. Thus, excessive pyds is required to ensure the purity of compounds **1–4**.

Table 1  
Crystallographic data for compounds 1–4

|  | 1                           | 2                           | 3                           | 4                           |
|--|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Crystal system                         | Monoclinic                  | Monoclinic                  | Monoclinic                  | Monoclinic                  |
| Space group                            | $C2/c$                      | $C2/c$                      | $C2/c$                      | $C2/c$                      |
| Empirical formula                      | $C_{37}H_{30}In_4N_2O_{25}$ | $C_{39}H_{34}In_4N_2O_{25}$ | $C_{39}H_{34}In_4N_2O_{25}$ | $C_{39}H_{32}In_4N_2O_{25}$ |
| Formula weight                         | 1361.92                     | 1389.96                     | 1389.96                     | 1387.95                     |
| $a$ , Å                                | 18.664(3)                   | 18.446(12)                  | 18.576(11)                  | 18.7360(12)                 |
| $b$ , Å                                | 14.4433(19)                 | 14.413(9)                   | 14.424(8)                   | 14.459                      |
| $c$ , Å                                | 17.573(3)                   | 17.527(12)                  | 17.601(11)                  | 17.5216(12)                 |
| $\beta$ , deg                          | 114.680(6)                  | 114.228(5)                  | 114.536(5)                  | 114.764(2)                  |
| $V$ , Å <sup>3</sup>                   | 4304.3(1)                   | 4249.6(4)                   | 4290.0(3)                   | 4310.2(4)                   |
| $Z$                                    | 4                           | 4                           | 4                           | 4                           |
| $D_{\text{calcd}}$ , g/cm <sup>3</sup> | 2.102                       | 2.173                       | 2.152                       | 2.139                       |
| $\mu$ , mm <sup>-1</sup>               | 2.213                       | 2.244                       | 2.223                       | 2.212                       |
| $R_1(I > 2\sigma(I))$                  | 0.0665                      | 0.0796                      | 0.0704                      | 0.0326                      |
| $wR_2$ (all data)                      | 0.1159                      | 0.1836                      | 0.1202                      | 0.0789                      |

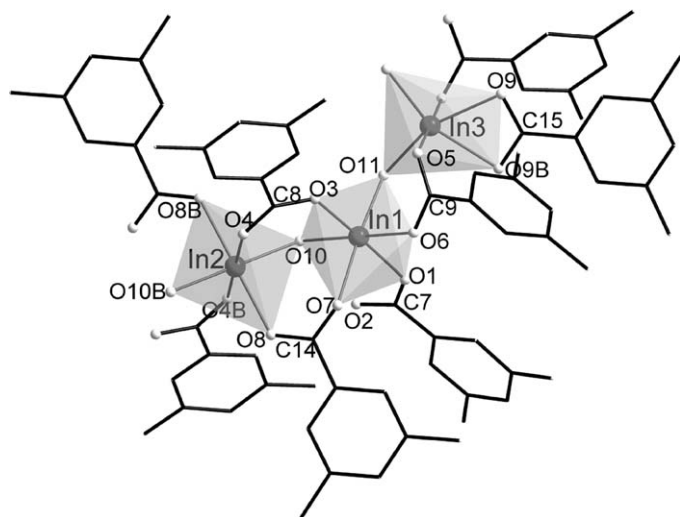


Fig. 1. View of the coordination environments of In(III) centers in compound 4.

### 3.2. Description of structure

Since four compounds have the same host frameworks, compound 4 is selected to represent their structures. Three indium atoms in 4 are each bonded by six oxygen atoms from four carboxyl and two  $\mu$ -OH groups (O10 and O11) to form a distorted octahedral geometry (Fig. 1). There are two kinds of indium coordination environments: for In1 and In3, two  $\mu$ -OH oxygen atoms occupy apical positions of octahedron in a *cis* mode; for In2, two  $\mu$ -OH oxygen atoms occupy apical positions of octahedron in a *trans* mode. The average In–O distance is 2.154 Å, compatible to those observed in other  $In^{III}$ –carboxylate complexes [11,12]. Bond valence sum (BVS) calculation [17] confirms that all indium ions have the oxidation state of +3. BVS is also applied for O10 and O11, giving the result of 1.17 and 1.25, which confirms that both are actually  $\mu$ -OH groups. Interestingly, each  $InO_6$  octahedron is connected to two adjacent  $InO_6$  octahedra by  $\mu$ -OH groups through corner-

sharing, resulting in an infinite In–O–In–O– chain like a sinusoidal curve (Fig. 2). The octahedra are severely tilted with angles of 117.6(2)° (In1–O10–In2) and 126.2(2)° (In1–O11–In3), very far from 180° for the perfect linear In–O–In–O chains. Arrangement of nine consecutive  $InO_6$  octahedra completes a period of the sinusoidal curve. The crest and the trough of sinusoidal curve are invariably occupied by In3 atoms which are coordinated by one chelating bidentate carboxyl unit (O9–C15–O9B) of a kind of  $btc^{3-}$  groups ( $btc-B$ ). The other two bidentate carboxyl units (O7–C14–O8 and their symmetry equivalent atoms) of  $btc-B$  each bonds to two indium atoms (In1 and In2) belonging to another chain. In this way  $btc-B$  ligands act as the bridges to connect chains into a layer substructure (Fig. 2).

The  $btc-A$  ligands interlink the layers. One carboxyl group (O3–C8–O4) of  $btc-A$  ligand bidentately attaches to a chain in a layer, while the other two carboxyl groups (O1–C7–O2 and O5–C9–O6), adopting monodentate and bidentate fashions, respectively, link to two chains in another layer (Fig. 3). The carboxyl arm (O5–C9–O6) is out of the  $btc-A$  benzene ring plane with a dihedral angle of 44.1°. Layers pack in the way of ABAB that neighboring layers are related by the half unit cell translation along crystallographic  $b$ -axis direction. The interactions between layers and  $btc-A$  groups result in a 3-D framework containing 1-D tunnels (Fig. 4) with approximate sizes of  $9.797 \times 8.917 \text{ Å}^2$  calculated from the centroid-to-centroid distances between the benzene rings of opposite  $btc^{3-}$  groups. The length 9.797 Å is also the distance between the two neighboring layers. Protonated organic guests (Hdpea) and free water molecules are located in the tunnels and form hydrogen bonds with the host framework [O12...N1(N1') 2.692, 2.868 Å; O12...O11 2.691 Å; O12...O2 2.986 Å]. For compounds 1–3, their two guest molecules, one neutral L and one cation HL, are located in approximately the above-mentioned position of Hdpea in the tunnel of 4 forming hydrogen bonding with free water molecules [N1...O12 2.692–2.871 Å]. And the guest water

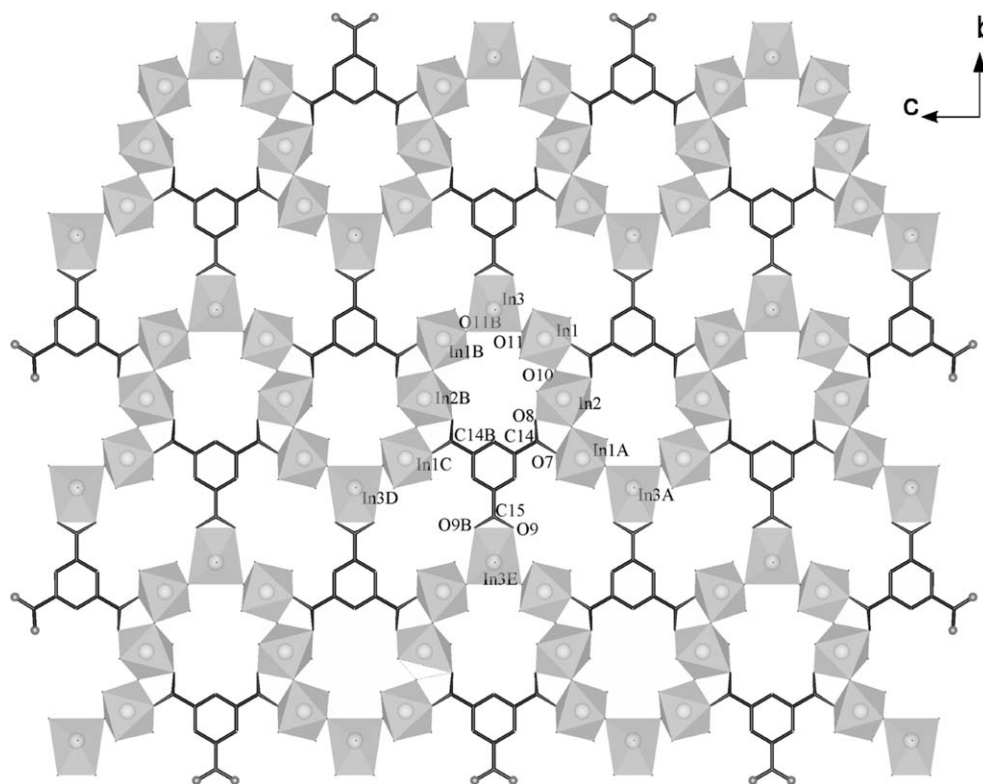


Fig. 2. The layer formed through the octahedral chains shaping like sinusoidal curve. The coordination environments on btc-B ligands binding in **4** can be clearly seen. The btc-A ligands are not shown for clarity. Selected bond lengths (Å): In1A–O7 2.193(3), In1–O10 2.121(3), In1–O11 2.110(3), In2–O10 2.081(3), In2–O8 2.219(3), In3–O11 2.044(3), In3E–O9 2.255(3). Symmetry code: A  $1-x, 1-y, 1-z$ ; B  $1-x, y, 1.5-z$ ; C  $x, 1-y, 0.5+z$ ; D  $1-x, 1-y, 2-z$ ; E  $x, -1+y, z$ .

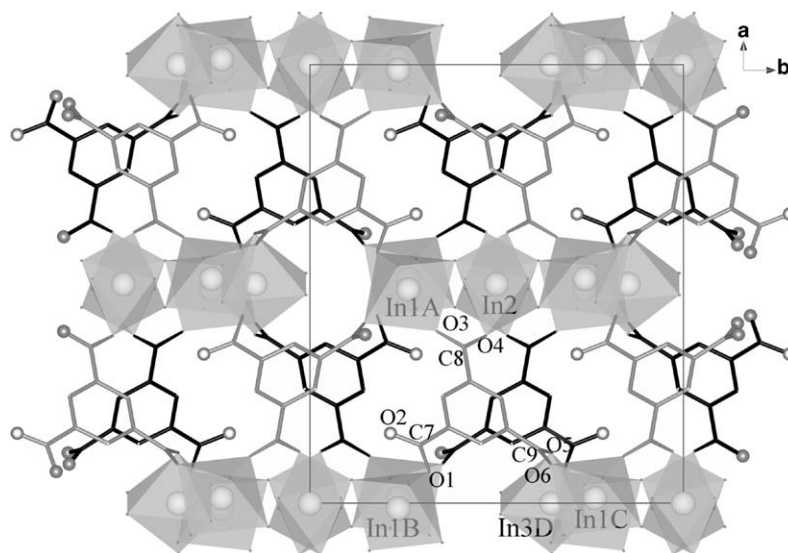


Fig. 3. The arrangement of alternate octahedral layers and btc-A gives a 3-D framework in **4**. The btc-B ligands and guest molecules are not shown for clarity. Selected bond lengths (Å): In1A–O3 2.137(3), In1B–O1 2.106(3), In1C–O6 2.164(3), In2–O4 2.179(3), In3D–O5 2.189(4). Symmetry code: A  $1-x, 1-y, 1-z$ ; B  $0.5-x, -0.5+y, 0.5-z$ ; C  $-0.5+x, 1.5-y, -0.5+z$ ; D  $0.5-x, 1.5-y, 1-z$ .

molecules also form hydrogen bonds with the host frameworks [O12...O11 2.748–2.765 Å; O12...O2 2.777–2.812 Å for **1–3**]. All of compounds **1–4** have highly open architectures since the accessible volumes within their

crystals are more than 36% as calculated by PLATON [18]. Compounds **1–4** represent an unprecedented anionic framework since no analogous has been reported in the literatures.

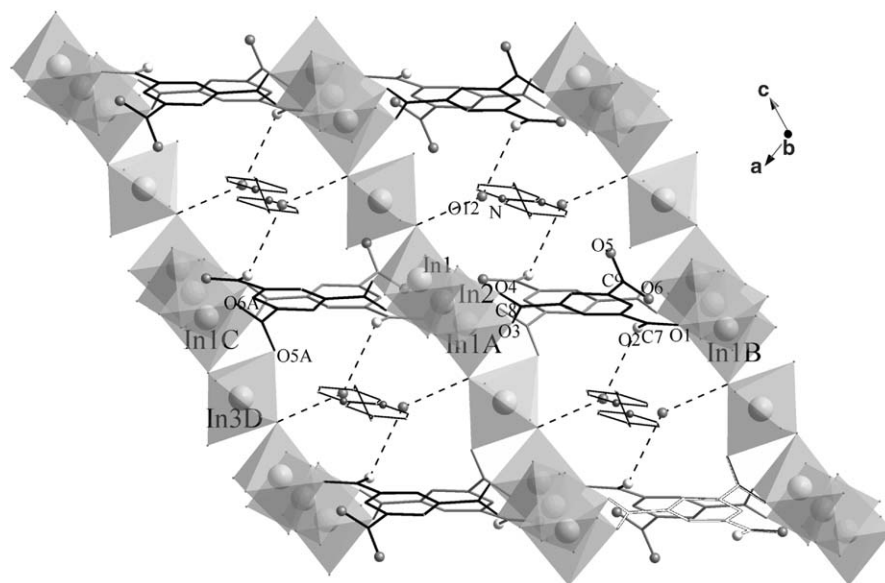


Fig. 4. Layers interlink through btc-A groups to generate a 3-D network with 1-D tunnels in **4**. The hydrogen bonds are displayed as dash lines. The uncoordinated O2 atoms are displayed as light gray balls. The btc-B groups are not shown for clarity. Symmetry code: A  $1-x, 1-y, 1-z$ ; B  $0.5-x, -0.5+y, 0.5-z$ ; C  $1.5-x, -0.5+y, 1.5-z$ ; D  $0.5+x, -0.5+y, z$ .

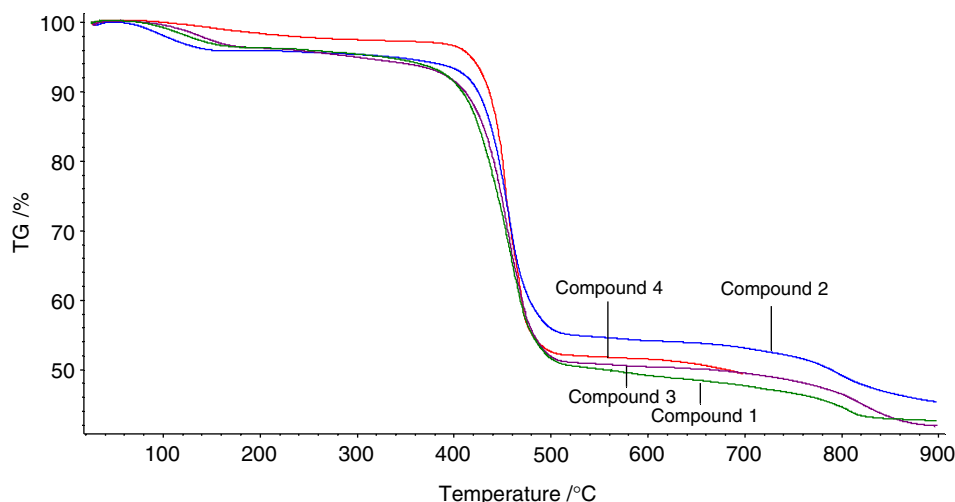


Fig. 5. TG curves of compounds **1–4** under N<sub>2</sub>.

### 3.3. Thermal analysis and ion-exchange properties

TG data for compounds **1–4** under flowing nitrogen atmosphere are shown in Fig. 5. The losses of weight with heating for **1–4** are concentrated into two major stages. The first stages occurring from room temperature to 150 °C correspond to the loss of three water molecules per formula unit (found: 3.5–4.0% for **1–4**, calculated ca.4.0%). Then, the weight kept nearly constant from 150 to 400 °C. In the second stage (400–480 °C), these compounds began to lose organic guests and, finally, their frameworks collapsed with the further simultaneous removal of organic cations and btc<sup>3-</sup> units.

In ion-exchange experiments, each crystalline sample (about 20 mg) of **1–4** was immersed in an aqueous solution of KCl, SrCl<sub>2</sub>, or BaCl<sub>2</sub> (10 mL, 1.0 M) in a 20-mL flask kept a constant temperature of 60 °C for 1 day. The exchanged products were filtered off, washed with distilled water three times, and then dried in air. Elemental analysis results [19] indicate that protonated pyds cations in **1–3** can be exchanged with the above-mentioned inorganic ions reflected by the decrease in C and N contents. The cation-exchanged products of **1–3** were also characterized by XRD. The XRD patterns confirm that the frameworks of **1–3** remain unchanged after Hpyds guests were replaced, as shown in Fig. 6 for some results. Exchange of Hdpea



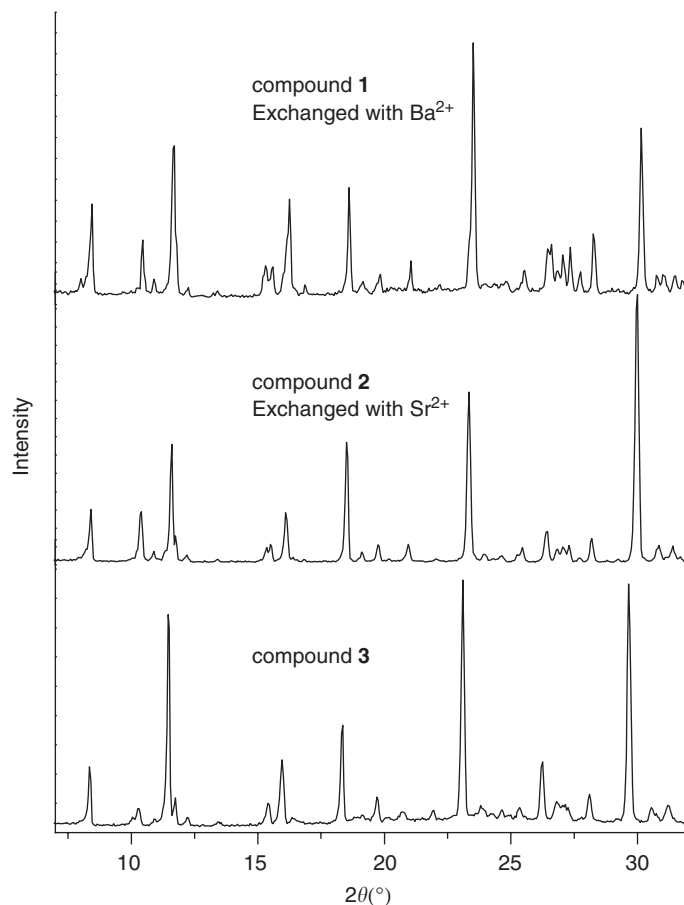


Fig. 6. XRD patterns for samples of 1–3 with or without cation-exchanged.

cations of **4** with the above inorganic ions is difficult based on slight changes in C, N and H contents for ion-exchanged product of **4**.

#### 4. Conclusions

Copolymerization of H<sub>3</sub>btc with indium ions under hydrothermal condition gives a 3-D anionic channel framework. The indium ions are linked by bridges forming In–O–In chains in compounds **1–4**. The protonated pyds (Hpy<sup>+</sup>, 2-Hpic<sup>+</sup>, 4-Hpic<sup>+</sup>, and Hdpea<sup>+</sup>) located at the channels act as counter ions to balance the negative charge frameworks. They can be exchanged by K<sup>+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup> cations. However, the organic guest cation Hdpea<sup>+</sup> at the channel is too large to be exchanged by inorganic cations. The sizes of guest molecules play an important role in the exchange ability of its parent compound.

#### Acknowledgments

This work was supported by the grants of National Nature Science Foundation of China, and Nature Science Foundation of Fujian Province. We thank Professor Jiutong Chen for technical assistance and discussions.

#### References

- [1] (a) H.L. Li, M. Eddaoudi, M. O’Keeffe, O.M. Yaghi, *Nature* 402 (1999) 276;  
(b) O.M. Yaghi, G. Li, H.L. Li, *Nature* 378 (1995) 703.
- [2] (a) S.I. Noro, S. Kitagawa, M. Kondo, K. Seki, *Angew. Chem. Int. Ed.* 39 (2000) 2082;  
(b) H.J. Choi, T.S. Lee, M.P. Suh, *Angew. Chem. Int. Ed.* 38 (1999) 1405.
- [3] (a) K.S. Min, M.P. Suh, *J. Am. Chem. Soc.* 122 (2000) 6834;  
(b) O.M. Yaghi, H. Li, *J. Am. Chem. Soc.* 118 (1996) 295.
- [4] (a) J.S. Seo, D.M. Whang, H.Y. Lee, S.I. Jun, J.H. Oh, Y.J. Jeon, K.M. Kim, *Nature* 404 (2000) 982;  
(b) T. Sawaki, Y. Aoyama, *J. Am. Chem. Soc.* 121 (1999) 4793.
- [5] (a) M. Albrecht, M. Lutz, A.L. Spek, G. van Koten, *Nature* 406 (2000) 970;  
(b) J.A. Real, E. Andrés, M.C. Munõz, M. Julve, T. Granier, A. Bousseksou, F. Varret, *Science* 268 (1995) 265.
- [6] (a) T.J. Prior, M.J. Rosseinsky, *Chem. Commun.* (2001) 495;  
(b) T.J. Prior, D. Bradshaw, S.J. Teat, M.J. Rosseinsky, *Chem. Commun.* (2003) 500;  
(c) M.J. Plater, M.R. St. J. Foreman, E. Coronado, C.J. Gómez-García, A.M.Z. Slawin, *J. Chem. Soc. Dalton Trans.* (1999) 4209.
- [7] (a) K.E. Holmes, P.F. Kelly, M.R.J. Elsegood, *Dalton Trans.* (2004) 3488;  
(b) X.J. Li, R. Cao, D.F. Sun, Y.Q. Sun, W.H. Bi, Y.Q. Wang, M.C. Hong, *Chin. J. Struct. Chem.* 23 (2004) 1017;  
(c) C.J. Kepert, M.J. Rosseinsky, *Chem. Commun.* (1998) 31.

- [8] (a) J.C. Dai, X.T. Wu, Z.Y. Fu, C.P. Cui, S.M. Hu, W.X. Du, L.M. Wu, H.H. Zhang, R.Q. Sun, *Inorg. Chem.* 41 (2002) 1391; (b) J. Fan, H.F. Zhu, T.A. Okamura, W.Y. Sun, W.X. Tang, N. Ueyama, *New J. Chem.* 27 (2003) 1409; (c) J. Kim, B.L. Chen, T.M. Reineke, H.L. Li, M. Eddaoudi, D.B. Moler, M. O'Keeffe, O.M. Yaghi, *J. Am. Chem. Soc.* 123 (2001) 8239; (d) M.J. Plater, R.A. Howie, A.J. Roberts, *Chem. Commun.* (1997) 893.
- [9] (a) C. Daiguebonne, O. Guillou, K. Boubekeur, *Inorg. Chim. Acta.* 304 (1999) 161; (b) C. Daiguebonne, O. Guilloa, Y. G  rault, A. Lecerf, K. Boubekeur, *Inorg. Chim. Acta* 284 (2000) 139; (c) C. Daiguebonne, Y. G  rault, F. Le Dret, O. Guillou, K. Boubekeur, *J. Alloys Compd.* 344 (2002) 179; (d) C. Daiguebonne, Y. G  rault, O. Guillou, A. Lecerf, K. Boubekeur, P. Batail, M. Kahn, O. Kahn, *J. Alloys Compd.* 275 (1998) 50.
- [10] C. Serre, C. F  rey, *J. Mater. Chem.* 12 (2002) 3053.
- [11] B. Gomez-Lor, E. Gutierrez-Puebla, M. Iglesias, M.A. Monge, C. Ruiz-Valero, N. Snejko, *Inorg. Chem.* 41 (2002) 2429.
- [12] (a) Z.Z. Lin, F.L. Jiang, L. Chen, D.Q. Yuan, M.C. Hong, *Inorg. Chem.* 44 (2005) 73; (b) Z.Z. Lin, J.H. Luo, M.C. Hong, R.H. Wang, L. Han, Y. Xu, R. Cao, *J. Solid State Chem.* 177 (2004) 2494.
- [13] (a) Z.Z. Lin, F.L. Jiang, L. Chen, D.Q. Yuan, Y.F. Zhou, M.C. Hong, *Eur. J. Inorg. Chem.* 1 (2005) 77; (b) Z.Z. Lin, L. Chen, F.L. Jiang, M.C. Hong, *Inorg. Chem. Commun.* (2005) 199; (c) Z.Z. Lin, F.L. Jiang, D.Q. Yuan, L. Chen, Y.F. Zhou, M.C. Hong, *Eur. J. Inorg. Chem.* 10 (2005) 1927.
- [14] G.M. Sheldrick, SHELXS97, Program for Crystal Structure Solution, University of G  ttingen, G  ttingen, Germany, 1997.
- [15] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of G  ttingen, G  ttingen, Germany, 1997.
- [16] P.V.D. Sluis, A.L. Spek, *Acta Crystallogr. A* 46 (1990) 194.
- [17] N.E. Brese, M. O'Keeffe, *Acta Crystallogr. B* 47 (1991) 192.
- [18] L. Spek, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, Netherlands, 1999.
- [19] Elemental analyses for cation exchanged samples: for  $K^+$ -exchanged sample of **1**: C, 28.65; N, 0.98; H, 2.35 for the  $Sr^{2+}$ -exchanged sample of **1**: C, 29.90; N, 1.44; H, 2.40; for  $Ba^{2+}$ -exchanged sample of **1**: C, 29.70; N, 1.44; H, 2.56; for  $K^+$ -exchanged sample of **2**: C, 29.43; N, 1.10; H, 2.19; for  $Sr^{2+}$ -exchanged sample of **2**: C, 29.66; N, 1.12; H, 2.45; for  $Ba^{2+}$ -exchanged sample of **2**: C, 29.12; N, 1.14; H, 2.16; for  $K^+$ -exchanged sample of **3**: C, 29.33; N, 0.97; H, 3.00.