DOI: 10.1002/ejic.200701060

Syntheses, Structures, and Characterizations of Two New Indium(III) Compounds from 1D ···In–OH–In–OH··· Chains and Pyridinedicarboxylic Ligands

Zhengang Guo,[a,b] Yafeng Li,[a] Wenbing Yuan,[a] Xiandong Zhu,[a] Xinfa Li,[a] and Rong Cao*[a]

Keywords: Indium / Self-assembly / Luminescence

The self-assembly of In_2O_3 with 2,5-pyridinedicarboxylic acid (2,5-H_2PDC) and 3,5-pyridinedicarboxylic acid (3,5-H_2PDC) generates two hybrid inorganic–organic compounds $[In(OH)(2,5\text{-PDC})]_n$ (**1**) and $[In_2(OH)_2(3,5\text{-PDC})_2(H_2O)]_n$ (**2**), respectively. The two compounds have been characterized by IR, XRPD, elemental analysis, and photoluminescent studies. The structure of **1** consists of corner-sharing $InNO_5$ octahedra and 2,5-PDC ligands to form 2D frameworks with thermal stability up to ca. 347 °C. The 3D framework of **2** contains corner-sharing InN_2O_4 octahedra and InO_7 decahedra with a 406 nm emission at 77 K. Both of the compounds possess similar one-dimensional ···In–OH–In–OH··· inorganic chains.

Introduction

During the past two decades the rational design and characterization of hybrid inorganic–organic compounds have undergone rapid development. The attraction of this field is justified by both the fascinating structures and topologies,[1] and the potential applications in the areas of catalysis,[2] magnetism,[3] luminescence,[4] gas storage,[5] and nonlinear optical materials.[6]

In order to obtain the designed and predictable frameworks and properties, chemists choose various systems with different metal ions and diverse organic moieties for each purpose.[7] As functional metal centers, indium ions attract more and more attention as a result of their fantastic coordination properties and special chemical characteristics arising from their variable coordination geometry and coordination numbers.[8] On the one hand indium can be used in organic chemistry,[9] on the other hand it can perform a good candidate in inorganic-assembly chemistry. Up to now, a series of articles have described the syntheses of indium coordination polymers.[10] However, much of the work so far has focused mainly on the systems arising from aromatic carboxylic ligands. Until recently, little attention has been devoted to indium hybrid organic–inorganic materials with nitrogen-donor multicarboxylate ligands.[11] Therefore we chose a system of 2,5-H_2PDC and 3,5-H_2PDC multifunctional carboxylic acids with indium ions in order to perform the self-assembly of indium ions with multidentate nitrogen-donor ligands. Compounds 2,5-H_2PDC and 3,5-H_2PDC give rise to a rich coordination geometry as a result of several possible coordination modes of the two carboxylic groups, such as bridging, chelating, and monodentate modes, as well as the potential coordinating nitrogen donor.[11a,12]

Herein we wish to report the syntheses, luminescence, X-ray characterizations, and the thermal stabilities of two new compounds $[In(OH)(2,5\text{-PDC})]_n$ (**1**) and $[In_2(OH)_2(3,5\text{-PDC})_2(H_2O)]_n$ (**2**), which were prepared from In_2O_3 and 2,5-H_2PDC and 3,5-H_2PDC by hydrothermal reactions, respectively. It is worth noting that both of the two compounds comprise similar secondary building units (SBUs) of ···In–OH–In–OH··· zigzag chains, which have already been documented in aromatic carboxylic polymers of indium.[8b] However, to the best of our knowledge, compounds **1** and **2** are the first aromatic nitrogen-donor carboxylates of indium that are built up of one-dimensional ···In–OH–In–OH··· inorganic chains.

Results and Discussion

Structural Descriptions

$[In(OH)(2,5\text{-PDC})]_n$ (1)

Compound **1** crystallized in the space group *Iba*2 with the flack polarity parameter $x = -0.010$, su. = 0.048, in

---

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences
Fuzhou, Fujian 350002, China
Fax: +86-591-83714946
E-mail: rcao@ms.fjirsm.ac.cn
[b] Graduate University of the Chinese Academy of Sciences
Beijing 100039, China

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

which the indium atoms are polymerized through the 2,5-PDC ligands to yield two-dimensional frameworks. As illustrated in Figure 1, each asymmetric unit comprises one hexacoordinate In^{III} center, one hydroxy group, and one 2,5-PDC ligand. The indium metal atom interacts with one nitrogen atom, two μ_2-OH groups, and three oxygen atoms from three independent 2,5-PDC ligands in a distorted octahedral environment. The carboxylic In–N distance and In–O bond range, 2.225(3) and 2.063(3)–2.289(3) Å, respectively, are comparable to those reported for other indium-oxygen and indium-nitrogen donor compounds.[10,11] The neighboring InNO$_5$ octahedra share the axial μ_2-OH groups along the [001] direction leading to one-dimensional SBUs of ···In–OH–In–OH··· zigzag chains. The In–OH–In angle is 129.85(1)° and the observed distance of the indium atom to the μ_2-OH groups is 2.063(3) Å, which is similar to the typical distance of In–OH.[8b] Moreover, these one-dimensional inorganic chains are linked by 2,5-PDC ligands in the [010] direction to form a two-dimensional framework (Figure 2, a). Each 2,5-PDC ligand connects three indium atoms (structure a, Scheme 1), with the nitrogen donor and monodentate carboxylic group chelating one indium atom and the other carboxylic group bridging two indium atoms. Finally, the μ_2-OH groups are hydrogen bonded to monodentate carboxyl oxygen atoms (Figure 2, b) from adjacent two-dimensional frameworks [O(1)–O(5A) distance: 2.748(3) Å; symmetry code: A –*x*, –*y*, *z*],[7b] leading to a three-dimensional supermolecule (Figure 2, c).

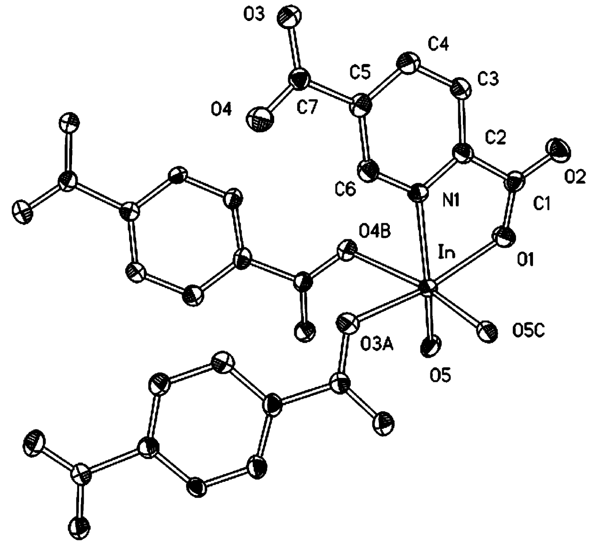
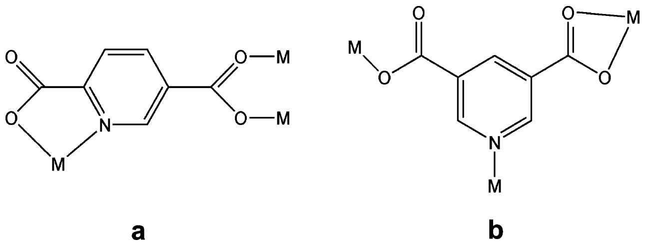
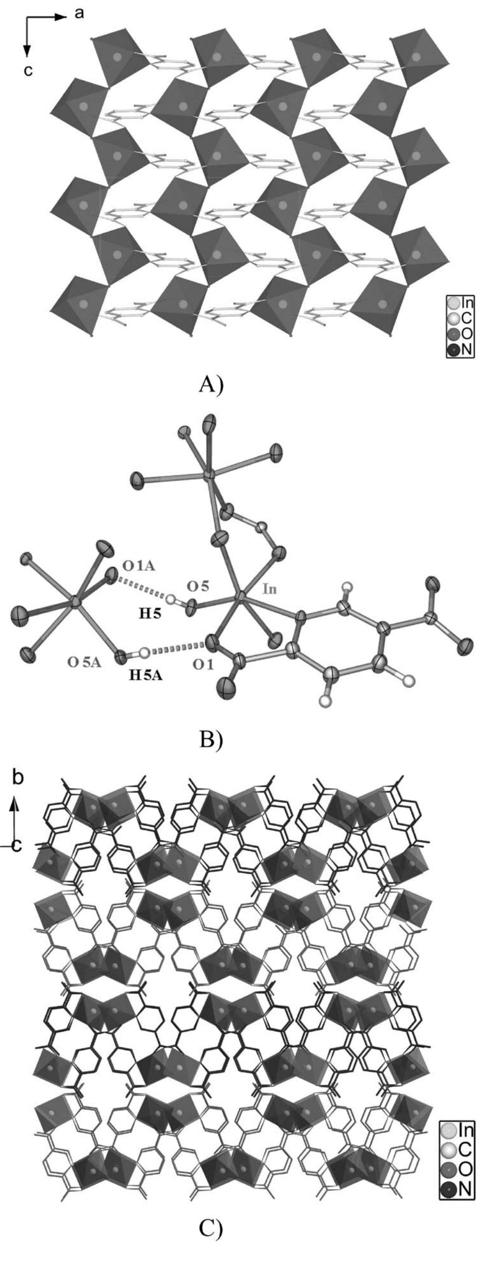


Figure 1. The coordination environment around In^{III} in compound **1** represented by thermal ellipsoids drawn at the 50% probability level.



Scheme 1. Coordination modes of the 2,5-H$_2$PDC and 3,5-H$_2$PDC ligands.



A)

B)

C)

Figure 2. View of the 2D layer in compound **1** in the [010] direction (a). Details of H-bond interactions (dotted lines) for compound **1** with thermal ellipsoids at the 50% probability level (b). Symmetry codes: A –*x*, –*y*, *z*. Packing of the 2D framework of compound **1** along the [001] direction (c).

[In$_2$(OH)$_2$(3,5-PDC)$_2$(H$_2$O)]$_n$ (2)

An X-ray diffraction study reveals that compound **2** belongs to the space group *C*2/*c* and possesses a three-dimensional framework consisting of six-coordinate and seven-coordinate dinuclear clusters. As shown in Figure 3, each asymmetric unit is composed of one μ_2-OH group, one 3,5-PDC ligand, half a water molecule as well as two halves of crystallographically independent indium atoms. The coordination sphere of the In1 atom can be described as a distorted InO_7 decahedron with two μ_2-OH groups on the vertical points, and one water molecule and four oxygen atoms from two chelate carboxylic groups on the plane. In contrast, the In2 atom is coordinated with two μ_2-OH groups in the axial direction, and two N atoms and two O atoms from monodentate carboxylic groups diagonally on the plane to form the InN_2O_4 octahedra. Two kinds of polyhedrons, InN_2O_4 octahedra and InO_7 decahedra, are corner-shared through the μ_2-OH groups to furnish 1D ···In–OH–In–OH··· zigzag chains. The In–OH–In angles [129.85(1)° for compound **1** and 142.69(8)° for **2**] are similar to those found in aromatic carboxylates of indium with 1D ···In–OH–In–OH··· inorganic chains.[8b,10c] In addition, the water molecules interact with the In1 atom to form hydrogen bonds with the monodentate carboxyl oxygen atom [Ow–O(4A) distance: 2.745(3) Å; symmetry code: A $x - 1/2$, $-y - 1/2$, $z - 1/2$] (Figure 4, a). Furthermore, each 3,5-PDC ligand arranges three ···In–OH–In–OH··· chains with the μ3 mode (structure b, Scheme 1) into the three-dimensional structure (Figure 4, b).

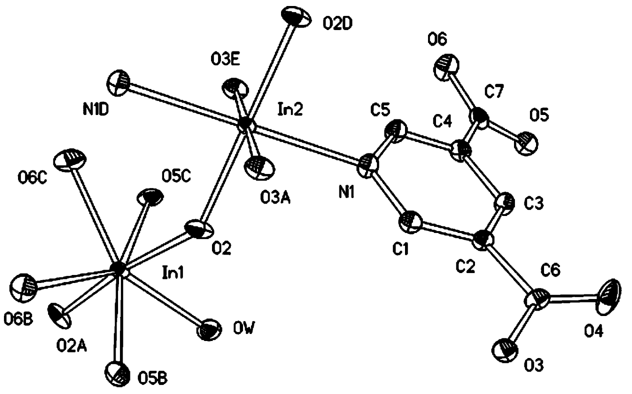
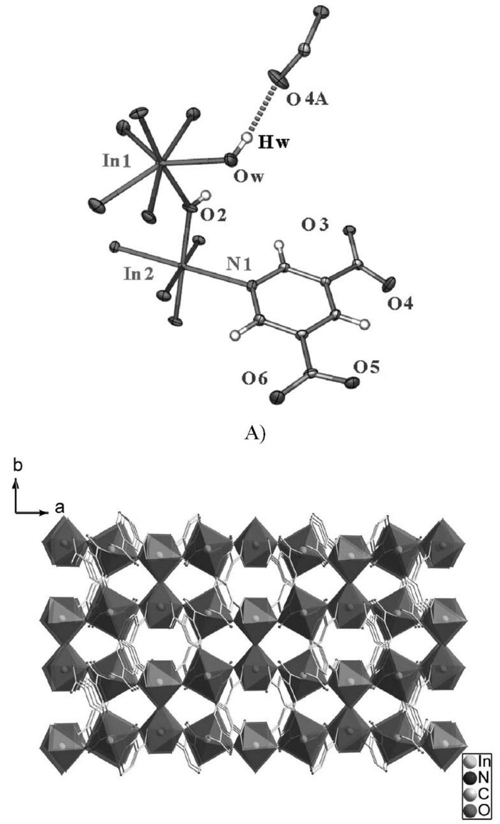


Figure 3. The coordination environment around In^{III} in compound **2** with the thermal ellipsoid at the 50% probability level. Symmetry-equivalent atoms are labeled with an additional letter.



A)

B)

Figure 4. Details of H-bond interactions (dotted lines) for compound **2** with thermal ellipsoids at the 50% probability level (a). Symmetry code: A $x - 1/2$, $-y - 1/2$, $z - 1/2$. Packing of the InN_2O_4 octahedra (green) and InO_7 decahedra (red) of compound **3** along the [001] direction (b).

Characterization of Vibrational Spectra

In the IR spectrum of compound **1** a strong absorption at 3130 cm^{-1} is attributed to the presence of an OH group. The bands at 1572 and 1410, 1343 cm^{-1} are due to the antisymmetric and symmetric stretching vibrations of the carboxylate groups, respectively. As shown in Figure 2 (b), the hydrogen bonds between the μ_2-OH groups and the monodentate carboxyl oxygen atoms cause the split of the antisymmetric stretching vibrations.[13] In the IR spectrum of compound **2** the broad band at 3380 cm^{-1} testifies to the existence of water molecules. The antisymmetric and symmetric stretching vibrations at 1567 and 1408, 1350 cm^{-1}, respectively, indicate that the carboxylate groups employ the chelating and monodentate coordination geometry. As illustrated in Figure 4 (a), the broad band at 3380 cm^{-1} arises from the hydrogen bonds between the coordinated water and the monodentate carboxyl oxygen atom, which is in accordance with the crystal structure.

Thermal Stability Analyses

The thermal gravimetric analyses (TGA) of the compounds were investigated on crystalline samples under 20 mL min^{-1} flowing nitrogen, while increasing the temperature at a rate of 15°min^{-1} from 35 to 900 °C. The TGA curve of compound **1** (Figure 5) shows high stability up to 347 °C. The weight loss (found 44.94%, calculated 44.15%) from 347 to 500 °C indicates the decomposition of the organic ligands leading to $In(OH)_3$. Then $In(OH)_3$ loses water to yield the final residue of In_2O_3 (found 43.74%, calculated 46.75%).[10a] The TGA curve of compound **2** (Figure 5) shows the first weight loss (found 3.05%, calculated 2.95%) between ca. 145 and 278 °, which is in accordance with the loss of H_2O molecules. The second weight loss (found 40.92%, calculated 42.85%) from 278 to 500 °C indicates the decomposition of the organic ligands leading to $In(OH)_3$. Then $In(OH)_3$ loses water to yield the final residue of In_2O_3 (found 43.82%, calculated 45.37%).[10a] The presence of $In(OH)_3$ during the decomposition of the two compounds was confirmed by energy dispersive X-ray spectroscopy (EDS). After heating the two compounds to 500 °C the EDS results show that no C and N are observed and that the molar ratio of O to In is about 3:1 in the residues (Figure S1).

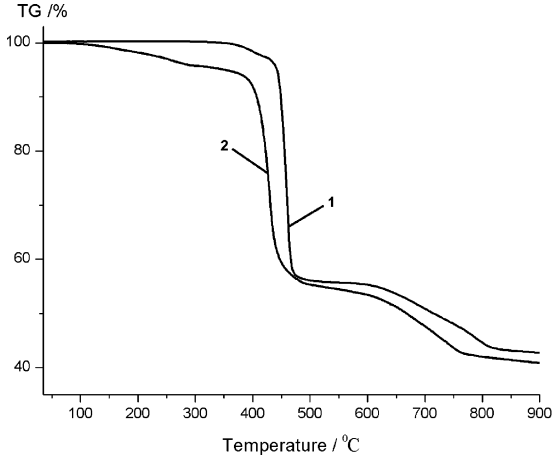


Figure 5. TGA curves for compound **1** and compound **2**.

Photoluminescence Properties

The photoluminescent spectra of compounds **1** and **2** were recorded at 77 K. As shown in Figure 6, excitation of compound **1** at 355 nm produces a blue emission with a peak maximum at 471 nm. The luminescent properties of hybrid inorganic–organic compounds are usually assigned to ligand-to-metal charge transfers (LMCT), metal-to-ligand charge transfers (MLCT), metal-centered transitions, or interligand π–π* transitions. Taking into account the emission of 2,5-H_2PDC centered at 392 nm,[12c,14] the emission of compound **1** may originate from the ligand-to-metal charge transfer (LMCT), a process similar to the photoluminescence of transitional metal zinc(II) compounds with carboxylic acid.[10c,15] The emission band of compound **2** ranges from 350 to 450 nm with the maximum emission at 406 nm (λ_{ex} = 306 nm). The photoluminescent properties of 3,5-H_2PDC (λ_{max} = 380 nm) were measured for comparison. The emission may be related to the charge transfer between indium(III) and the 3,5-H_2PDC ligands.[10c,11c,16]

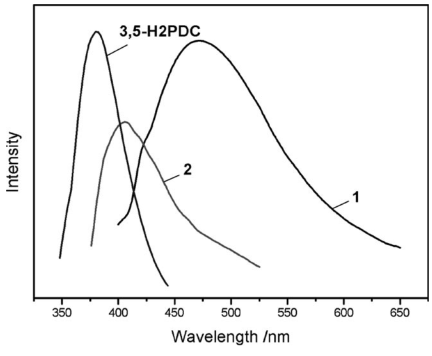


Figure 6. Solid-state emission spectra of compound **1**, **2** at 77 K and 3,5-H_2PDC at room temperature.

Conclusions

In summary, we have successfully constructed two new hybrid inorganic–organic compounds, which are constructed from $InNO_5$ or InN_2O_4 and InO_7 polyhedra with shared μ_2-OH vertices. To the best of our knowledge, compounds **1** and **2** exemplify the first aromatic nitrogen-donor carboxylates of indium based on the assembly of infinite one-dimensional ···In–OH–In–OH··· zigzag building blocks. It is reasonable to believe that the foregoing results are important to enrich the metal–organic assemblies of indium. Present work is in progress to use this approach to synthesize homo- or heterometallic metal–organic frameworks with InN_xO_y polyhedrons.

Experimental Section

Materials and General Methods: All reagents were commercially available and used without further purification. Infrared spectra were recorded with a Magna 750 FT-IR spectrophotometer using KBr pallets. The elemental analyses of C, H, and N were determined using a Perkin–Elmer 240C elemental analyzer. X-ray powder diffraction (XRPD) patterns of the samples were recorded with an X-ray diffractometer (RIGAKU-DMAX2500). Thermal analyses were recorded using a NETZSCH STA 449C unit. Fluorescence spectroscopy of two compounds was performed with an Edinburgh Analytical instrument FLS920 at 77 K. The energy dispersive X-ray spectroscopy (EDS) was performed with a JEOL-6700F SEM instrument.

Synthesis: Solid In_2O_3 (27.8 mg, 0.1 mmol) was added to a solution of pyridinedicarboxylic acid (16.7 mg, 0.1 mmol) and $HClO_4$ (0.031 mmol) in deionized water (15 mL), the mixture was sealed in a hydrothermal reaction vessel and heated at 165 °C for 72 h. After cooling at a rate of 3 °C/h to room temperature, air-stable white crystals were obtained and then washed with ethanol. The final pH of the reaction system was ca. 2.68. Yield 10 mg, 33.7% (compound **1** based on In); 12 mg, 39.2% (compound **2** based on In). Elemental analysis (%) for $C_7H_4InNO_5$ (296.93): calcd. C 28.32, H 1.36, N 4.72; found C 28.30, H 1.40, N 4.70. For $C_7H_5InNO_{5.5}$ (305.94): calcd. C 27.48, H 1.65, N 4.58; found C 27.42, H 1.70, N 4.50. IR (KBr) for compound **1**: $\tilde{\nu}$ = 3130 (br. s), 1572 (s), 1410 (m), 1343 (s), 1227 (w), 827 (w), 765 (w), 737 (w), 651 (w) cm^{-1}. IR (KBr) for compound **2**: $\tilde{\nu}$ = 3380 (br. s), 1567 (s), 1408 (m), 1350 (s), 843 (w), 768 (w), 743 (w), 650 (w) cm^{-1}.

X-ray Crystallographic Studies: Measurements of compounds **1** and **2** were collected with a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo-K_α (radiation λ = 0.71073 Å) at room temperature. The absorption corrections were performed by using the CrystalClear software package.[17] The structures were solved by direct methods with the SHELXL-97 program package.[18] All data were refined by full-matrix least-squares minimizations of $\sum(F_o - F_c)^2$ with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms belonging to the water molecules and μ_2-OH groups were found in the electron-density map. The other hydrogen atoms were generated geometrically (C–H 0.95 Å). The crystallographic data and structure determination summaries for compounds **1** and **2** are listed in Table 1. The selected bond lengths and angles for two compounds are listed in Table 2.

CCDC-659856 (for **1**) and -659857 (for **2**) contain the supplementary crystallographic data for this paper. These data can be ob-

Table 1. Crystal data and structure determination summary for compounds **1** and **2**.

	1	**2**
Formula	$C_7H_4InNO_5$	$C_{14}H_{10}In_2N_2O_{11}$
M_r [g mol^{-1}]	296.93	611.88
Crystal size [mm]	0.25 × 0.17 × 0.12	0.30 × 0.21 × 0.15
Crystal system	orthorhombic	monoclinic
Space group	*Iba*2	*C*2/*c*
a [Å]	12.632(1)	16.137(1)
b [Å]	20.088(2)	9.864(1)
c [Å]	6.217(1)	11.158(1)
β [°]		111.800(3)
V [Å^3]	1577.7(2)	1649.2(2)
Z	8	8
D_c [g cm^{-3}]	2.500	2.464
μ [mm^{-1}]	2.989	2.868
F(000)	1136	1176
T [K]	298(2)	298(2)
λ(Mo-K_α) [Å]	0.71073	0.71073
Reflections collected	5902	6158
Unique reflections	1765	1182
R_{int}	0.0269	0.0157
Parameters	129	140
S on F_2	1.097	1.061
R_1 [$I > 2\sigma(I)$][a]	0.0239	0.0161
wR_2 [$I > 2\sigma(I)$][b]	0.0488	0.0372
R_1 (all data)	0.0266	0.0170
wR_2 (all data)[b]	0.0500	0.0376
$\Delta\rho_{min}$ and $_{max}$ [e Å^{-3}]	1.047 and –0.370	1.238 and –0.503

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

Table 2. Selected bond lengths [Å] and angles [°] for compounds **1** and **2**.[a]

Compound **1**			
In–O5	2.063(3)	In–O3B	2.182(3)
In–O5A	2.103(3)	In–N1	2.225(3)
In–O1	2.148(3)	In–O4C	2.289(3)
O5–In–O5A	103.39(8)	O1–In–N1	75.0(1)
O5–In–O1	93.0(1)	O3B–In–N1	90.9(1)
O5A–In–O1	90.8(1)	O5–In–O4C	83.9(1)
O5–In–O3B	102.2(1)	O5A–In–O4C	162.4(1)
O5A–In–O3B	85.8(1)	O1–In–O4C	104.9(1)
O1–In–O3B	164.8(1)	O3B–In–O4C	77.0(1)
O5–In–N1	154.9(1)	N1–In–O4C	78.3(1)
O5A–In–N1	98.8(1)		
Compound 2			
In1–O2	2.124(1)	In2–O2	2.089(1)
In1–OW	2.184(2)	In2–O3E	2.161(1)
In1–O6B	2.255(2)	In2–N1	2.322(2)
In1–O5B	2.311(2)		
O2A–In1–O2	172.1(1)	O6C–In1–O5B	139.8(1)
O2–In1–OW	86.04(4)	O2–In1–O5C	80.9(1)
O2–In1–O6B	92.2(1)	O5B–In1–O5C	162.5(1)
OW–In1–O6B	138.14(4)	O2–In2–O3E	87.7(1)
O2–In1–O6C	93.7(1)	O2–In2–O3F	92.3(1)
O6B–In1–O6C	83.7(1)	O2–In2–N1D	88.4(1)
O2–In1–O5B	97.9(1)	O2–In2–N1	91.6(1)
OW–In1–O5B	81.25(4)	O3E–In2–N1	86.7(1)
O6B–In1–O5B	57.5(1)	O3F–In2–N1	93.3(1)

[a] Symmetry codes, for **1**: A –*x*, *y*, *z* + 1/2; B *x* – 1/2, –*y* + 1/2, *z*; C –*x* + 1/2, –*y* + 1/2, *z* – 1/2. For **2**: A –*x*, *y*, –*z* + 3/2; B –*x* + 1/2, *y* + 1/2, –*z* + 3/2; C *x* – 1/2, *y* + 1/2, *z*; D –*x* + 1/2, –*y* + 1/2, –*z* + 2; E *x*, –*y*, *z* – 1/2; F –*x* + 1/2, *y* + 1/2, –*z* + 5/2.

tained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): The EDS patterns (Figure S1) and X-ray powder diffraction (XRPD) patterns (Figure S2).

Acknowledgments

This work was financially supported by the 973 Program (2006CB932900/03), the Chinese National Science Foundation (NSF) (90206040, 20325106, 50472021, 20731005), National Science Foundation of Fujian Province (2005HZ01-1), Fujian Key Laboratory of Nanomaterials (2006L2005), "The Distinguished Overseas Scholar", "One Hundred Talents" and Key projects from CAS. We thank Professor Zhongning Chen for helpful discussions.

---

[1] a) M. C. Hong, Y. J. Zhao, W. P. Su, R. Cao, M. Fujita, Z. Y. Zhou, A. S. C. Chan, *J. Am. Chem. Soc.* **2000**, *122*, 4819–4820; b) R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, K. Kindo, Y. Mita, A. Matsuo, M. Kobayashi, H. Chang, T. C. Ozawa, M. Suzuki, M. Sakata, M. Takata, *Science* **2002**, *298*, 2358–2361; c) C. R. Woods, M. Benaglia, F. Cozzi, J. S. Siegel, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1830–1834; d) J. M. Vincent, C. Philouze, I. Pianet, J. B. Verlhac, *Chem. Eur. J.* **2000**, *6*, 3595–3599; e) L. Pan, B. S. Finkel, X. Y. Huang, J. Li, *Chem. Commun.* **2001**, 105–106; f) F. A. A. Paz, Y. Z. Khimyak, A. D. Bond, J. Rocha, J. Klinowski, *Eur. J. Inorg. Chem.* **2002**, 2823–2828; g) K. Barthelet, J. Marrot, D. Riou, G. Férey, *Angew. Chem. Int. Ed.* **2002**, *41*, 281–284.

[2] a) B. Gomez-Lor, E. Gutiérrez-Puebla, M. Lglesias, M. A. Monge, C. Ruiz-Valero, N. Snejko, *Inorg. Chem.* **2002**, *41*, 2429–2432; b) R. Q. Zou, H. Sakurai, S. Han, R. Q. Zhong, Q. Xu, *J. Am. Chem. Soc.* **2007**, *129*, 8402–8403.

[3] a) M. Riou-Cavellec, C. Lesaint, M. Nogués, J. Grenéche, G. Férey, *Inorg. Chem.* **2003**, *42*, 5669–5674; b) S. M. Humphrey, P. T. Wood, *J. Am. Chem. Soc.* **2004**, *126*, 13236–13237; c) A. B. Gaspar, V. Ksenofontov, V. Martinez, M. C. Muñoz, J. A. Real, P. Gütlich, *Eur. J. Inorg. Chem.* **2004**, 4770–4773; d) S. C. Xiang, X. T. Wu, J. J. Zhang, R. B. Fu, S. M. Hu, X. D. Zhang, *J. Am. Chem. Soc.* **2005**, *127*, 16352–16353.

[4] a) J. Tao, J. X. Shi, M. L. Tong, X. X. Zhang, X. M. Chen, *Inorg. Chem.* **2001**, *40*, 6328–6330; b) J. Pang, E. J. P. Marcotte, C. Seward, R. S. Brown, S. N. Wang, *Angew. Chem. Int. Ed.* **2001**, *40*, 4042–4045; c) H. J. Tracy, J. L. Mullin, W. T. Klooster, J. A. Martin, J. Haug, S. Wallace, I. Rudloe, K. Watts, *Inorg. Chem.* **2005**, *44*, 2003–2011; d) L. H. Gao, M. Guan, K. Z. Wang, L. P. Jin, C. H. Huang, *Eur. J. Inorg. Chem.* **2006**, 3731–3737.

[5] a) C. D. Wu, W. B. Lin, *Angew. Chem. Int. Ed.* **2005**, *44*, 1958–1961; b) M. M. Dincă, J. Long, *J. Am. Chem. Soc.* **2005**, *127*, 9376–9377; c) D. F. Sun, S. Q. Ma, Y. X. Ke, D. J. Collins, H. C. Zhou, *J. Am. Chem. Soc.* **2006**, *128*, 3896–3897.

[6] W. Chen, Z. R. Li, D. Wu, Y. Li, C. C. Sun, F. L. Gu, Y. Aoki, *J. Am. Chem. Soc.* **2006**, *128*, 1072–1073.

[7] a) P. M. Forster, A. R. Burbank, C. Livage, G. Férey, A. K. Cheetham, *Chem. Commun.* **2004**, 368–369; b) Z. G. Guo, R. Cao, X. J. Li, D. Q. Yuan, W. H. Bi, X. D. Zhu, Y. F. Li, *Eur. J. Inorg. Chem.* **2007**, 742–748.

[8] a) J. Y. Sun, L. H. Weng, Y. M. Zhou, J. X. Chen, Z. X. Chen, Z. C. Liu, D. Y. Zhao, *Angew. Chem. Int. Ed.* **2002**, *41*, 4471–4473; b) E. V. Anokhina, M. Vougo-Zanda, X. Q. Wang, A. J. Jacobson, *J. Am. Chem. Soc.* **2005**, *127*, 15000–15001; c) W. Fujita, K. Awaga, R. Kondo, S. Kagoshima, *J. Am. Chem. Soc.* **2006**, *128*, 6016–6017.

[9] a) B. E. Eichler, N. J. Hardman, P. P. Power, *Angew. Chem. Int. Ed.* **2000**, *39*, 383–385; b) M. Veith, S. Hill, V. Huch, *Eur. J. Inorg. Chem.* **1999**, 1343–1350.

[10] a) Z. Z. Lin, F. L. Jiang, L. Chen, D. Q. Yuan, Y. F. Zhou, M. C. Hong, *Eur. J. Inorg. Chem.* **2005**, *77*–81; b) B. Gómez-Lor, E. Gutiérrez-Puebla, M. Iglesias, M. A. Monge, C. Ruiz-Valero, N. Snejko, *Chem. Mater.* **2005**, *17*, 2568–2573; c) Z. Z. Lin, F. L. Jiang, L. Chen, D. Q. Yuan, M. C. Hong, *Inorg. Chem.* **2005**, *44*, 73–76; d) Z. Z. Lin, F. L. Jiang, D. Q. Yuan, L. Chen, Y. F. Zhou, M. C. Hong, *Eur. J. Inorg. Chem.* **2005**, 1927–1931; e) Y. L. Wang, Q. Y. Liu, S. L. Zhong, *Acta Crystallogr., Sect. C* **2006**, *62*, m395–m397; f) C. Volkringer, T. Loiseau, *Mater. Res. Bull.* **2006**, *41*, 948–954; g) M. Vougo-Zanda, X. Q. Wang, A. J. Jacobson, *Inorg. Chem.* **2007**, *46*, 8819–8824; h) Z. Z. Lin, F. L. Jiang, L. Chen, C. Y. Yue, D. Q. Yuan, A. J. Lan, M. C. Hong, *Cryst. Growth Des.* **2007**, *7*, 1712–1715; i) Y. L. Liu, J. F. Eubank, A. J. Cairns, J. Eckert, V. Ch. Kravtsov, R. Luebke, M. Eddaoudi, *Angew. Chem. Int. Ed.* **2007**, *46*, 3278–3283.

[11] a) Y. L. Liu, V. Ch. Kravtsov, D. A. Beauchamp, J. F. Eubank, M. Eddaoudi, *J. Am. Chem. Soc.* **2005**, *127*, 7266–7267; b) F. Ramezanipour, H. Aghabozorg, A. Shokrollahi, M. Shamsipur, H. Stoeckli-Evans, J. Soleimannejad, S. Sheshmani, *J. Mol. Struct.* **2005**, *779*, 77–86; c) M. K. Pal, N. P. Kushwah, A. P. Wadawale, V. S. Sagoria, V. K. Jain, E. R. T. Tiekink, *J. Solid State Chem.* **2007**, *692*, 4237–4243.

[12] a) J. F. Eubank, R. D. Walsh, M. Eddaoudi, *Chem. Commun.* **2005**, 2095–2097; b) P. S. Wang, C. N. Moorefield, M. Panzer, G. R. Newkome, *Chem. Commun.* **2005**, 4405–4407; c) Y. G. Huang, B. L. Wu, D. Q. Yuan, Y. Q. Xu, F. L. Jiang, M. C. Hong, *Inorg. Chem.* **2007**, *46*, 1171–1176.

[13] Y. B. Go, X. Q. Wang, E. V. Anokhina, A. J. Jacobson, *Inorg. Chem.* **2005**, *44*, 8265–8271.

[14] Y. S. Song, B. Yan, Z. X. Chen, *J. Mol. Struct.* **2005**, *750*, 101–108.

[15] W. Y. Yang, H. Schmider, Q. G. Wu, Y. S. Zhang, S. N. Wang, *Inorg. Chem.* **2000**, *39*, 2397–2404.

[16] a) Z. Z. Lin, J. H. Luo, M. C. Hong, R. H. Wang, L. Han, R. Cao, *J. Solid State Chem.* **2004**, *177*, 2494–2498; b) X. Wang, T. L. Sheng, R. B. Fu, S. M. Hu, S. C. Xiang, L. S. Wang, X. T. Wu, *Inorg. Chem.* **2006**, *45*, 5236–5238.

[17] Molecular Structure Corporation and Rigaku, *CrystalClear Version 1.36*, MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo, Japan, **2000**.

[18] G. M. Sheldrick, *SHELXS 97*, *Program for Crystal Structure Solution*, University of Göttingen, Göttingen, **1997**.

Received: September 30, 2007