

Influence of Ligand Geometry on the Formation of In–O Chains in Metal-Oxide Organic Frameworks (MOOFs)

Marie Vougo-Zanda, Xiqu Wang, and Allan J. Jacobson*

Department of Chemistry, University of Houston, Houston, Texas 77204-5003

Received June 8, 2007

Three indium-oxide organic frameworks, $\text{In}_2\text{O}(1,3\text{-BDC})_2$, **1**; $\text{In}(\text{OH})(2,6\text{-NDC})(\text{H}_2\text{O})$, **2**; and $\text{In}(\text{OH})(2,7\text{-NDC})(\text{H}_2\text{O})$, **3** (BDC = benzene dicarboxylic acid and NDC = naphthalene dicarboxylic acid), were synthesized and characterized by thermogravimetric analysis, infrared spectroscopy, and single-crystal X-ray diffraction. Previously, we reported the structure of $\text{In}(\text{OH})(1,4\text{-BDC})\cdot(0.75\text{H}_2\text{BDC})$, **0**, where the framework is built by interconnecting In–OH–In chains with the BDC anions to form large diamond-shaped one-dimensional channels filled with guest molecules. Compounds **0–3** all contain In–O(H) chains, but the coordination and geometry depend on the nature of the dicarboxylate ligand. Compound **0** contains In–O octahedral centers that connect to form a single trans octahedral chain, while in compound **1**, they connect to form a more complex double chain of octahedra. Both compounds **2** and **3** contain chains of connected pentagonal bipyramidal $\text{InO}_6(\text{OH}_2)$ units. In **2**, these units share trans vertices that are cross-linked by chelating 2,6-NDC anions, whereas in compound **3**, cis vertices are shared to form chains that are linked by the 2,7-NDC anions.

Introduction

The synthesis and characterization of porous solids with either purely inorganic or organic–inorganic hybrid frameworks has been an area of rapid growth. Many new compounds have been synthesized and studied for possible application in, for example, catalysis, molecular separations, and gas storage.^{1–4} Early studies of purely inorganic frameworks such as zeolites have been extended to hybrid frameworks constructed from metal ions linked by organic ligands such as organo-phosphonates, sulfonates, and carboxylates. Metal-organic frameworks often have very large porosities, and the ability to modify their pore space with a wide range of functional groups can be used to introduce sorption selectivity.^{5–7}

Metal-oxide organic frameworks are a subgroup of metal-organic frameworks and are characterized by the presence of extended metal-oxide layers⁸ or metal-oxide chains⁶ in their structures. The extended metal-oxide $[-\text{O}-\text{M}-\text{O}-\text{M}-\text{O}-]_n^\infty$ components distinguish this class of compounds from those with isolated metal centers⁹ or small metal-oxide clusters.¹⁰ Several examples of metal-oxide organic frameworks containing metal-oxide layers or chains connected by bridging organic ligands, for example, 1,4-benzenedicarboxylate (BDC), have been reported. Férey and co-workers in a series of papers described the synthesis and structures of the $\text{M}(\text{OH})\text{BDC}$ phases where $\text{M} = \text{Al}, \text{V},$ and Cr ,^{7,11–12} and we have extended the series to include phases with $\text{M} = \text{In}, \text{Fe}, \text{Ga},$ and Y .^{13–16}

* To whom correspondence should be addressed. Telephone: (713) 743-2785. Fax: (713) 743-2787. E-mail: ajacob@uh.edu.

- (1) Davis, M. E. *Nature* **2002**, *417*, 813.
- (2) Hagman, P. J.; Hagman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.
- (3) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474.
- (4) Barton, T. J.; Bull, L. M.; Klempner, W. G.; Loy, D. A.; McEnaney, B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. *Chem. Mater.* **1999**, *11*, 2633.
- (5) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276.
- (6) Zheng, L.; Whitfield, T.; Wang, X.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 4528.
- (7) Serre, C.; Millange, F.; Thouvenot, C.; Nogues, M.; Marsolier, G.; Louer, D.; Férey, G. *J. Am. Chem. Soc.* **2002**, *124*, 13519.
- (8) Johnson, J. W.; Jacobson, A. J.; Rich, S. M.; Brody, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 5246–5247; *Rev. Chim. Miner.* **1982**, *19*, 420–431.
- (9) Lu, J.; Paliwala, T.; Lim, S. C.; Yu, C.; Niu, T.; Jacobson, A. J. *Inorg. Chem.* **1997**, *36*, 923–929.
- (10) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276–279.
- (11) Barthelet, K.; Marrot, J.; Riou, D.; Férey, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 281.
- (12) Loiseau, T.; Serre, C.; Huguenard, C.; Fink, G.; Taulelle, F.; Henry, M.; Bataille, T.; Férey, G. *Chem.—Eur. J.* **2004**, *10*, 1373.
- (13) Whitfield, T. R.; Wang, X.; Liu, L.; Jacobson, A. J. *Solid State Sci.* **2005**, *7*, 1096–1103.
- (14) Anokhina, E. V.; Vougo-Zanda, M.; Wang, X.; Jacobson, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 15000–15001.

In the present work, we report the synthesis and single-crystal structure determination of $\text{In}_2\text{O}(\text{1,3-BDC})_2$, **1**; $\text{In}(\text{OH})\text{-(2,6-NDC)}(\text{H}_2\text{O})$, **2**; and $\text{In}(\text{OH})(\text{2,7-NDC})(\text{H}_2\text{O})$, **3**, which are examples of metal-oxide organic frameworks containing metal-oxide chains connected by different dicarboxylate anions. We discuss the influence of the ligand geometry on the coordination of the In atoms and on the formation of the In–O chains.

Experimental Section

Materials and Methods. All reactants were reagent grade and used as purchased without further purification. Elemental analyses were performed by Galbraith Laboratories (Knoxville, Tennessee). Compound **1**, **2**, and **3** were first formulated through crystal structure determination, and then the compositions were confirmed by chemical and thermogravimetric analysis. The thermal decomposition behavior of compounds **1**, **2**, and **3** was determined by heating them in air at 3 °C/min on a TA Instruments thermogravimetric analyzer. X-ray powder diffraction indicated that the final residue is $\text{InO}_{1.5}$ for all three compounds. The IR spectra were recorded on a Galaxy Fourier transform infrared 5000 series spectrometer at room temperature in the range of 4000–400 cm^{-1} using the KBr pellet method. UV diffuse reflectance measurements were performed with a Cary 500 spectrophotometer. The absorption spectrum of the sample was approximated using the Kubelka–Munk function: $\{\alpha\}/\{S\} = \{(1 - R)^2\}/\{2R\}$, where R is the reflectance at a given wavelength, α is the absorption coefficient, and S is the scattering coefficient. The band gap (E_g) value is extracted from the $(\alpha/S)^2$ versus energy plot. E_g is taken as the point where the extrapolated linear portion of the plot intersects the energy axis at $(\alpha/S)^2 = 0$.

Synthesis of $\text{In}_2\text{O}(\text{1,3-BDC})_2$ (1**).** Compound **1** was synthesized from a mixture of indium metal (2 mmol), isophthalic acid (1 mmol), and deionized water (10 mL) in molar ratio of 2:1:560. The starting chemicals and deionized water were mixed into a hydrothermal reaction vessel and heated at 220 °C for 14 d. After quenching to room temperature, the product was filtered and washed with distilled water and dried at ambient temperature. The final product was a mixed phase containing excess beads of In metal that could easily be removed, a minor phase of an unidentified powder, and a major phase of light yellow crystals of $\text{In}_2(\text{O})(\text{C}_8\text{H}_4\text{O}_4)_2$, **1**, suitable for single-crystal X-ray analysis. Decreasing the reaction temperature to 200 °C resulted in a pure polycrystalline phase of $\text{In}_2(\text{O})(\text{C}_8\text{H}_4\text{O}_4)_2$, **1**, with some excess indium metal beads. Elem Anal.: In, 38.30% obs. (40.00% calcd); C, 33.51% obs. (33.45% calcd); H, 1.52% obs. (1.40% calc.). IR (KBr): 3430.8w(br), 1609.3s, 1573.6s, 1557.2s, 1482.0m, 1449.2s, 1422.6s, 1407.8s, 1322.0w, 1272.8w, 1160.0w, 1104.0w, 1080.9w, 1006.7w, 950.7w, 816.7w, 728.0s, 713.5m, 655.7w, 562.2m, 487.9w, 456.1m, 435.8m cm^{-1} . The IR spectrum of $\text{In}_2(\text{O})(\text{C}_8\text{H}_4\text{O}_4)_2$ exhibits characteristic bands of the dicarboxylate groups at $\sim 1450 \text{ cm}^{-1}$. The absence of any strong absorption bands at approximately 1700 cm^{-1} confirms the complete deprotonation of the carboxyl groups of the 1,3-BDC molecule.

Synthesis of $\text{In}(\text{OH})(\text{2,6-NDC})(\text{H}_2\text{O})$ (2**).** In a typical synthesis of **2**, indium nitrate (1 mmol), 2,6-naphthalic acid (1 mmol), HF (48%, Merck, 0.02 mL), and deionized water (10 mL) in their molar ratios of 1:1:0.5:560 were mixed into a hydrothermal reaction vessel

and heated at 200 °C for 3 d. After quenching to room temperature, the product was filtered and washed with distilled water and dried at ambient temperature. The final product was a mixed phase containing unreacted 2,6-naphthalic acid, an unidentified powder, and light yellow crystals of $\text{In}(\text{OH})(\text{2,6-NDC})(\text{H}_2\text{O})$ suitable for single-crystal X-ray analysis. The naphthalic acid was removed by washing with pyridine, and then the crystals were physically separated from the small amount of unidentified powder. Elem Anal.: In, 31.20% obs. (31.54% calcd); C, 40.54% obs. (39.56% calcd); H, 2.45% obs. (2.47% calcd). IR (KBr): 3506.0w(br), 3390.3w(br), 3253.3w(br), 1670.1m, 1602.6m, 1548.6s, 1490.7m, 1427.1s, 1357.6m, 1303.7m, 1193.7w, 1141.7w, 1041.7w, 973.9w, 931.5m, 817.7m, 788.7s, 646.0w, 580.5w, 541.9w, 486.0m cm^{-1} . The IR spectrum of $\text{In}(\text{OH})(\text{2,6-NDC})(\text{H}_2\text{O})$ shows a broad band in the area 3100–3600 cm^{-1} , indicating the presence of the OH and H_2O group vibrations. The absence of a band at $\sim 1700 \text{ cm}^{-1}$ confirms the complete deprotonation of the carboxyl groups of $\text{H}_2\text{-NDC}$.

Synthesis of $\text{In}(\text{OH})(\text{2,7-NDC})(\text{H}_2\text{O})$ (3**).** Compound **3** was synthesized from a mixture of indium metal (2 mmol), 2,7-naphthalenedicarboxylic acid dimethyl ester (1 mmol), and deionized water (10 mL) in their molar ratio of 2:1:560. The starting chemicals and deionized water were mixed into a hydrothermal reaction vessel and heated at 200 °C for 15 d. After quenching to room temperature, the product was filtered and washed with distilled water and dried at ambient temperature. The final product was a mixed phase containing excess beads of In metal, a minor phase of unidentified powder, and a major phase of light yellow crystals of $\text{In}(\text{OH})(\text{2,7-NDC})(\text{H}_2\text{O})$ suitable for single-crystal X-ray analysis. After removal of the indium beads, the crystals were physically separated from the small amount of unidentified powder. Elem Anal.: In, 30.90% obs. (31.54% calcd); C, 38.55% obs. (39.56% calcd); H, 2.33% obs. (2.47% calcd). IR (KBr): 3488.6w(br), 3386.4w(br), 3275.5w(br), 1669.1w, 1631.5w, 1590.m, 1542.8m, 1446.3s, 1390.4m, 1351.9s, 1236.2w, 1188.9w, 1150.3w, 1106.0w, 1036.6w, 959.4w, 942.1w, 865.9s, 797.4s, 768.5m, 660.5m, 615.2m, 574.7w, 536.1w, 478.3w cm^{-1} . The IR spectrum of $\text{In}(\text{OH})(\text{2,7-NDC})(\text{H}_2\text{O})$ shows a broad band in the area 3100–3600 cm^{-1} , indicating the presence of the OH and H_2O group vibrations. The absence of a band at $\sim 1700 \text{ cm}^{-1}$ confirms the complete deprotonation of the carboxyl groups of H_2NDC .

Crystallographic Studies. X-ray single-crystal analyses for **1**, **2**, and **3** were performed on a Siemens SMART platform diffractometer outfitted with an Apex II area detector and monochromatized graphite Mo K α radiation. The structures were solved by direct methods and refined using SHELXTL. The hydrogen atoms of the carboxylate ligands were generated geometrically and allowed to ride on their respective parent atoms. The hydrogen atoms of the OH and H_2O were located from difference maps and refined with atom distance constraints. Crystal data for compounds **1**, **2**, and **3** are summarized in Table 1. The structures are shown in Figures 1 and 2; compound **0** is included for comparison in Figures 3 and 4.

Results and Discussion

Crystal Structures. $\text{In}_2(\text{O})(\text{C}_8\text{H}_4\text{O}_4)_2$, **1.** The local coordination geometry around each indium atom in $\text{In}_2(\text{O})(\text{C}_8\text{H}_4\text{O}_4)_2$, **1**, is a slightly distorted octahedron of oxygen atoms. Each In^{3+} ion is coordinated to four oxygen atoms from four different carboxylate groups and to two oxygen atoms O(1) that are each coordinated to three other In atoms (see Figure 1).

(15) Vougo-Zanda, M.; Anokhina, E.; Duhovic, S.; Liu, L.; Wang, X.; Jacobson, A. J. Submitted.

(16) Vougo-Zanda, M.; Wang, X.; Jacobson, A. J. Unpublished results.

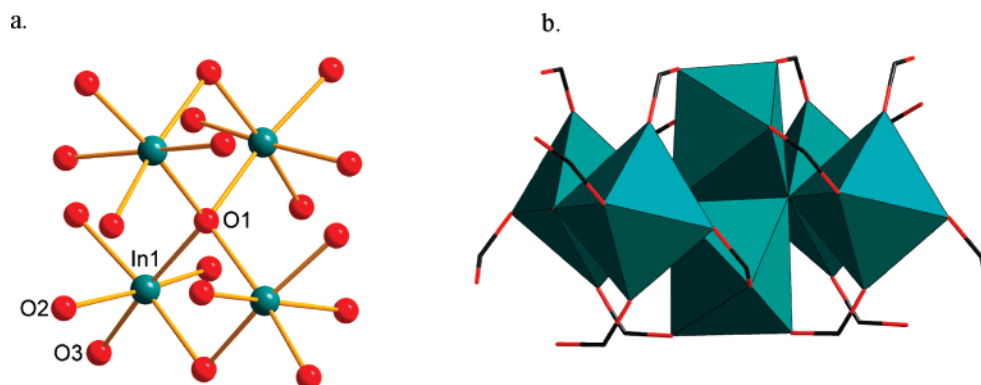


Figure 1. (a) The local coordination environment of the indium ion in **1** and (b) a polyhedral representation of part of the chain showing the bridging carboxylate ions.

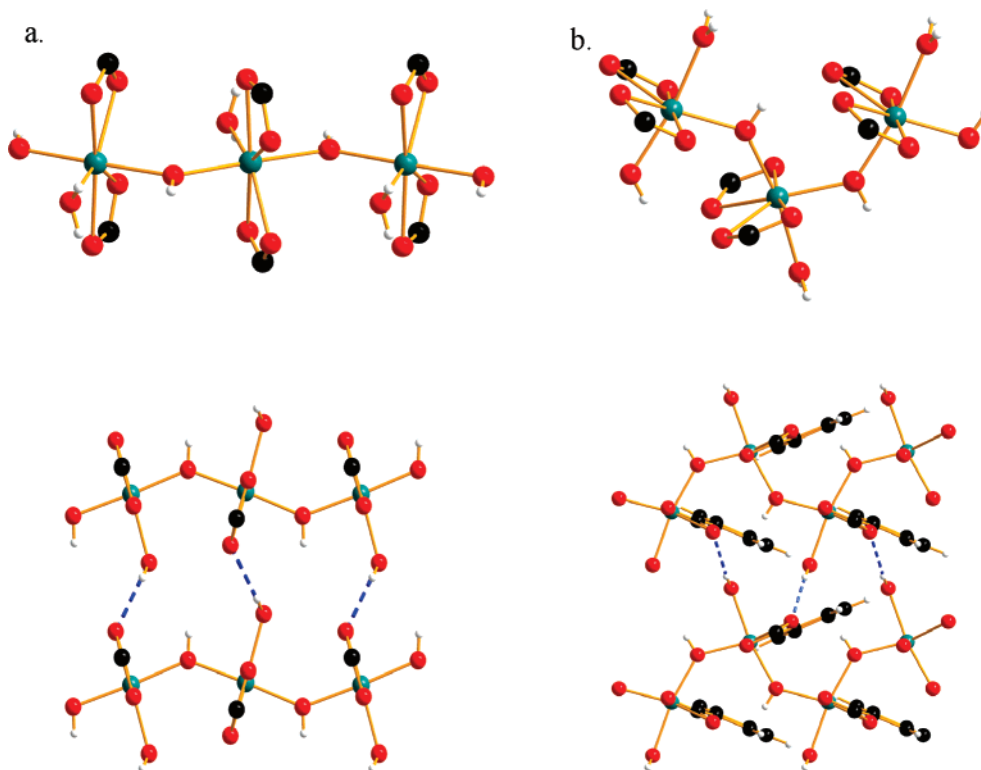


Figure 2. (a) The trans chain in $\text{In}(\text{OH})(2,6\text{-NDC})(\text{H}_2\text{O})$, (b) the cis chain in $\text{In}(\text{OH})(2,7\text{-NDC})(\text{H}_2\text{O})$. Hydrogen bonds between adjacent chains are shown as dotted blue lines.

The $\text{In}(1)\text{--O}(1)$ bond lengths between the tetrahedrally coordinated oxygen atoms and the In atoms are $2.1980(1)$ Å, and the other four In--O bond lengths are $\text{In}(1)\text{--O}(3) = 2.131(1)$ Å ($\times 2$) and $\text{In}(1)\text{--O}(2) = 2.165(1)$ Å ($\times 2$). Each InO_6 octahedron shares an edge with a neighboring octahedron to form In dimers. The dimers are connected to each other through O(1) to form double chains of In_2O along the c axis. Each In_2O chain is linked to four neighboring In_2O chains through the 1,3-BDC ligands to form the extended structure. Compound **1** decomposes in a single step (Figure 5a) between 450 and 500 °C, and the weight loss corresponds to the loss of one 1,3-BDC anion (51.94% measured, 51.61% calculated) per In atom.

$\text{In}(\text{OH})(2,6\text{-NDC})(\text{H}_2\text{O})$, **2.** The indium atom in $\text{In}(\text{OH})(2,6\text{-NDC})(\text{H}_2\text{O})$ (**2**) is seven-coordinated by five oxygen atoms from NDC, one oxygen atom from an --OH , and one from a water molecule and has approximately pentagonal

bipyramidal geometry. The axial hydroxyl oxygen atoms are shared with adjacent In atoms to form a trans chain (see Figure 2a). The carboxylate anions are chelating, and their oxygen atoms lie in the equatorial plane together with the oxygen atom from a coordinated water molecule. The equatorial In--O bond lengths are $\text{In}(1)\text{--O}(4)_\text{W} = 2.175(4)$ Å, $\text{In}(1)\text{--O}(1) = 2.247(3)$ Å ($\times 2$), and $\text{In}(1)\text{--O}(2) = 2.266(2)$ Å ($\times 2$), and the shorter axial bond lengths are $2.080(2)$ and $2.084(3)$ Å. The In--O pentagonal bipyramidal centers are linked by sharing trans hydroxyl groups to form bent $\cdots\text{In--OH--In--OH}\cdots$ chains with In--OH--In angles of $140.2(1)^\circ$. Four of the equatorial oxygen atoms are shared with the NDC anions where each carboxylic group is attached to the same In atom.

This connection mode results in the formation of a framework with no channels. In contrast, in $\text{Al}(\text{OH})\text{NDC}$, reported by Férey et al., each of the carboxylic groups of

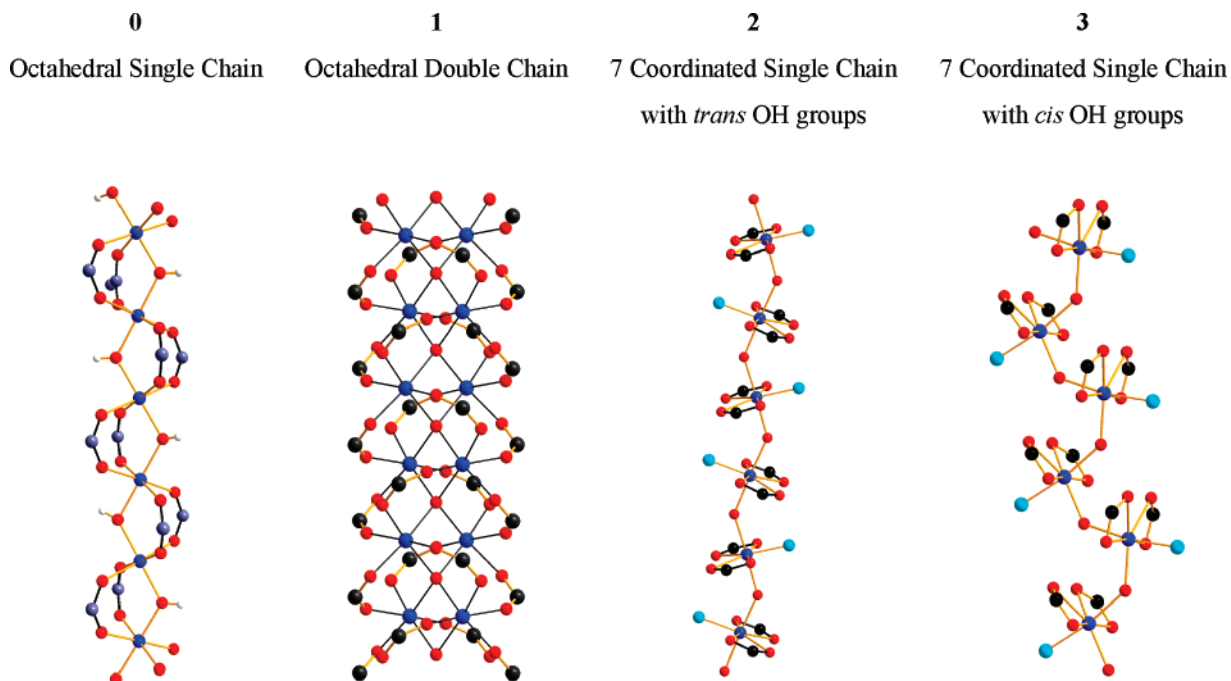


Figure 3. The In–O chains in compounds **0**, **1**, **2**, and **3**. The indium, oxygen, carbon, and hydrogen atoms are shown as blue, red, black, and white spheres, respectively. The coordinated water molecules are represented by blue spheres.

Table 1. Crystallographic Data for Compounds **1–3**

	1	2	3
chemical formula	In ₂ O(C ₈ H ₄ O ₄) ₂	In(OH)(C ₁₂ H ₆ O ₄)·(H ₂ O)	In(OH)(C ₁₂ H ₆ O ₄)·(H ₂ O)
Fw	574	364	364
cryst syst	tetragonal	orthorhombic	orthorhombic
space group	<i>P4₂/ncm</i>	<i>Pnma</i>	<i>Pmc2₁</i>
<i>a</i> , Å	16.0978(8)	7.8360(6)	12.339(2)
<i>b</i> , Å	16.0978(8)	25.456(2)	7.4473(12)
<i>c</i> , Å	5.9217(6)	5.7985(4)	6.0339(10)
<i>V</i> , Å ³	1534.5(2)	1156.7(2)	554.5(2)
<i>Z</i>	4	4	2
temp, K	293	293	293
ρ_c , g cm ⁻³	2.484	2.090	2.180
μ (Mo K α), mm ⁻¹	3.061	2.064	2.153
R1, wR2 [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0159, 0.0426	0.0273, 0.0667	0.0134, 0.0349
R1, wR2 (all data) ^a	0.0185, 0.0437	0.0290, 0.0675	0.0134, 0.0349

$${}^a R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, wR2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}.$$

the NDC ligand are attached to two consecutive octahedral metal centers, resulting in a 3D framework with accessible 1D channels.¹⁷ In **2**, The NDC ligand bridges the chains in a zigzag fashion to form a dense three-dimensional framework. The structure is further stabilized by the presence of hydrogen bonds (Figure 2a) between the coordinated water molecules and the carboxylate oxygen atoms [$O4_w \cdots O2 = 2.811(4)$ Å]. Thermal decomposition of **2** shows the loss of the framework water molecule in the temperature range of 100–150 °C (Figure 5b). The second weight loss between 400 and 500 °C corresponds to the loss of 1 mol of framework NDC (56.68% measured, 58.84% calculated). Compound **2** is an insulating material with a band gap at room temperature of 5.6 eV.

In(OH)(2,7-NDC)(H₂O), 3. In **3**, the local coordination geometry around the In atom is also pentagonal bipyramidal. Each In³⁺ is coordinated to two oxygen atoms, one from a

coordinated water molecule and the other from a hydroxyl group in the axial positions. Four oxygen atoms from two carboxylate groups and one hydroxyl oxygen atom occupy the equatorial positions.

The In–O distances are 2.0917(3) and 2.0902(3) Å for the In–OH bonds, 2.2142(3) Å for the In–OH₂ bonds, and 2.2500(2) and 2.3456(4) Å for the four In–O bonds from the carboxylate anions (see Figure 2b). The InO₄(OH)₂(OH₂) centers are linked by sharing *cis* hydroxyl groups to form $\cdots\text{In–OH–In–OH}\cdots$ zigzag chains with In–OH–In angles of 132.586(3)° and OH–In–OH angles of 103.966(3)°. The chains are connected through the 2,7-NDC ligands in the [100] direction to form a layer. The layers are linked through strong hydrogen bonds between H₂O molecules and carboxylate oxygen atoms [$O4_w \cdots O3 = 2.709(5)$ Å], thermogravimetric analysis (TGA) data show that the decomposition of compound **3** occurs in two steps (Figure 5c). The first weight loss in the temperature range of 200–300 °C corresponds to the removal of one water molecule from the

(17) Loiseau, T.; Mellot-Draznieks, C.; Muguerra, H.; Férey, G.; Haouas, M.; Taulelle, F. *C. R. Chim.* **2005**, *8*, 765.

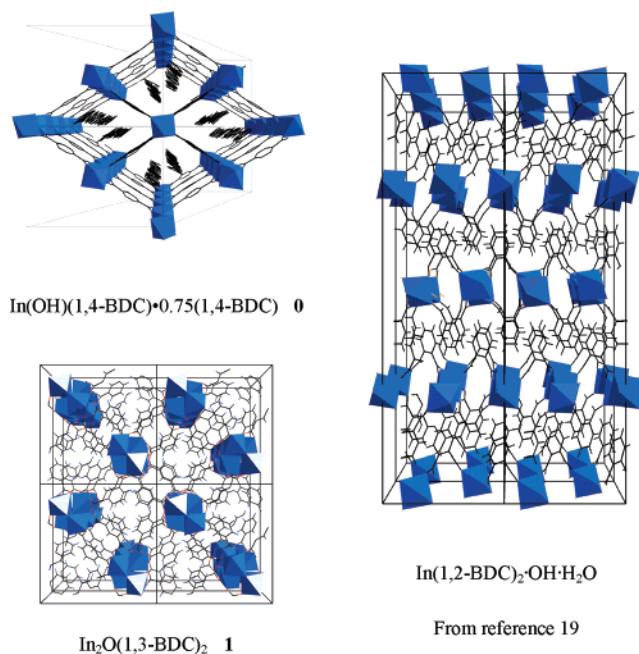


Figure 4. A comparison of the extended structures of 1,2-, 1,3-, and 1,4-InBDC compounds. The InO_6 octahedra are represented as blue polyhedra.

framework (4.47% measured, 4.94% calculated). The second weight loss between 300 and 475 °C corresponds to the loss of one framework 2,7-NDC (56.50% measured, 58.84%

calculated). Compound **3** is also an insulating material with a band gap at room temperature of 5.6 eV.

Discussion

Compounds **1**, **2**, and **3** along with the previously reported $\text{In(OH)(1,4-BDC)} \cdot (0.75\text{H}_2\text{BDC})$, **0**, all have indium-oxide organic frameworks, but each has a distinct extended metal-oxide chain with an arrangement that is determined by the geometry of the organic ligand. The various chain arrangements are summarized in Figure 3. In compound **0**, the axial oxygen groups of each InO_6 unit are shared by neighboring octahedra to form a single zigzag $\cdots\text{In-OH-In}\cdots$ chain.

In compound **1**, each In–O octahedral center shares an edge with a neighboring octahedron to form In dimers. The dimers are connected to each other through a tetrahedrally coordinated oxygen atom to form double chains of In_2O along the *c* axis. In compounds **2** and **3**, the In atoms are seven-coordinated to form pentagonal bipyramidal centers. In the case of **2**, the In–O centers are linked by sharing trans hydroxyl groups to form $\cdots\text{In-OH-In}\cdots$ chains and by sharing cis hydroxyl groups in the case of **3** to also form distorted single chains.

The differences between the various structures reflect primarily the geometrical arrangement of the two carboxylate groups. In compounds **0** and **1**, all of the carboxylate anion bridge between different InO_6 octahedra. The 180° angle between the carboxylate anions in 1,4-BDC results in the

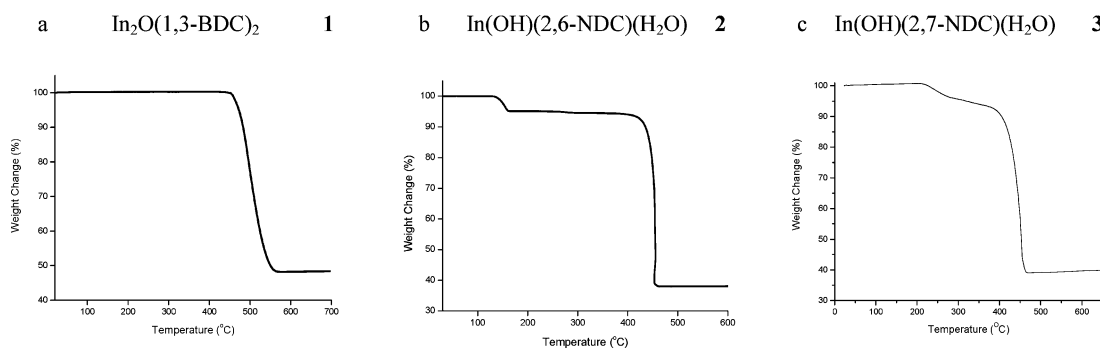


Figure 5. Thermogravimetric analysis results for compounds **1–3**.

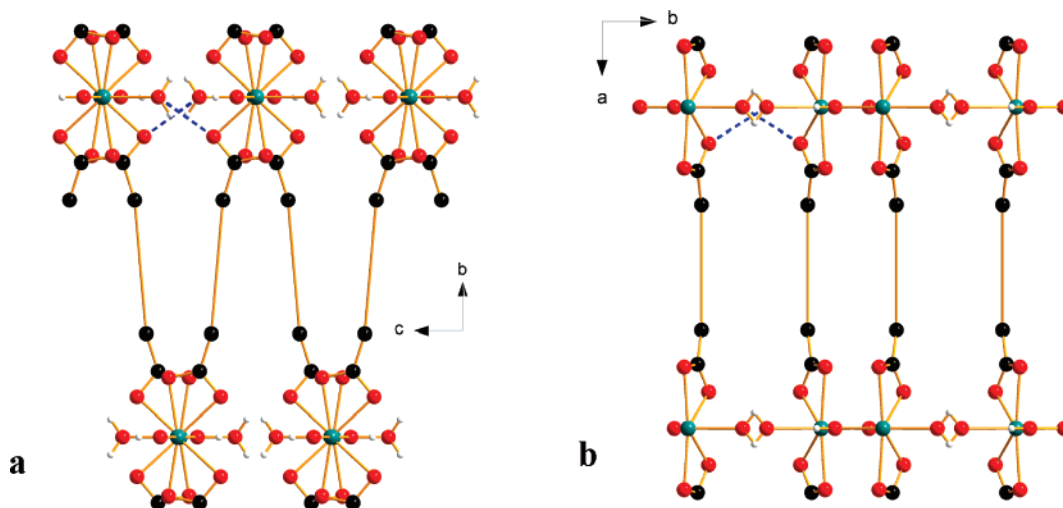


Figure 6. (a) The structures of $\text{In(OH)(2,6-NDC)(H}_2\text{O)}$ and (b) $\text{In(OH)(2,7-NDC)(H}_2\text{O)}$. Indium, oxygen, carbon, and hydrogen atoms are represented as green, red, black, and white spheres, respectively; hydrogen bonds are shown as dotted blue lines.

Table 2. A Survey of Indium BDC Compounds

compound	in CN	in connectivity	carboxylate	bridging ligand	OCO angle(s)	ref
InH(1,4-BDC) ₂	8	0	chelating		120.7	19
In(1,4-BDC) _{1.5} (bipy)	8	0	chelating		120.5, 120.0	20
In ₂ (OH) ₂ (1,4-BDC) ₂ (phen) ₂	6	tetramer	mono	2 × OH ⁻ (cis)	124.7, 126.7	20
In ₂ (OH) ₃ (1,4-BDC) _{1.5}	6	layer	bridging	3 × OH ⁻	126.4, 125.7, 124.4	21
In(OH)(1,4-BDC)0.75H ₂ BDC	6	chain	bridging	2 × OH ⁻ (trans)	126.0, 125.9	14
In ₂ F _{2.4} (OH) _{1.6} (1,4-BDC)·2.6H ₂ O	6	layer	bridging	4 × OH ⁻ , F ⁻	124.2	15
In ₂ (O)(1,3-BDC) ₂	6	chain	bridging	O ⁼	125.5	
In(1,2-BDC)(OH)(H ₂ O)	6	double chain	bridging, mono	OH ⁻	124.7, 125.1	18

characteristic diamond-shaped open framework shown in Figure 4. In contrast, the carboxylate groups in 1,3-BDC are at an angle of 120° to each other, and this leads to further condensation with the formation of a μ^4 oxide ion. Compound **1** is the only example of an indium-dicarboxylate chain structure that does not contain a bridging OH⁻ ion. In **1**, the aromatic rings are too far apart for π bonding; there is space between pairs of aromatic rings, but because of the tetragonal symmetry, adjacent pairs are orthogonal. Recently, the structure of In(OH)-1,2-BDC H₂O was reported.¹⁸ The 60° angle between the carboxylate groups further constrains the geometry. The In atom is six-coordinated by two hydroxyl ions that are shared between pairs of indium atoms, one water molecule, and three oxygen atoms from three different BDC anions, InO_{3/2}(OH)_{2/2}(H₂O)_{1/1}. Pairs of trans In···(OH)···In chains are connected by bridging dicarboxylate groups to form a double chain. One-half of the BDC anions have one unshared oxygen atom. The chains in the structure are connected by π - π interactions between the aromatic rings.

The structures of **2** and **3** are similar in several respects. Both contain indium atoms that are seven-coordinated by four oxygen atoms from two chelating NDC anions, one oxygen atom from a water molecule and two axial hydroxide ions that bridge adjacent indium atoms to form the chain. In both structures, the coordinated water molecule is strongly hydrogen-bonded to one carboxylate oxygen atom (see Figure 6). In **2**, the linear arrangement of the two carboxylate groups permits cross-linking of adjacent trans chains into a three-dimensional array, whereas the bent geometry of 2,7-NDC causes the structure to “fold up”; a cis geometry for the chain connections and a layer structure result. As apparent in the TGA data and bond lengths, the hydrogen bonding is stronger in **3** than in **2**.

Conclusion

The synthesis and crystal chemistry of indium dicarboxylates are now quite extensive. Examples are known with 6-, 7-, and 8-coordinated indium ions and with all coordination modes of the dicarboxylate ligand, namely, monodentate, and bidentate, bridging, and chelating. A survey of compounds with BDC ligands is given in Table 2. In the two 8-coordinated systems, the indium atoms are isolated from each other

by three chelating ligands; InH(1,4-BDC)₂ was obtained in N,N-dimethylformamide, whereas In(1,4-BDC)_{1.5}(bipy) was synthesized in water. It is likely that the chelating bipyridine stabilizes this structure since all of the other examples synthesized contain bridging oxide or hydroxide ions. Only 6- and 8-coordination numbers have been observed with BDC ligands, but 7-coordination is observed with NDC with the inclusion of one water molecule into the indium coordination sphere.

Other In compounds with benzene carboxylate ligands include In₂(BTC)₂(H₂O)₂·2H₂O and In₂(H₂BTEC)₂(OH)₂·2H₂O (where H₃BTC = 1,3,5-benzenetricarboxylic acid and H₄BTEC = 1,2,4,5-benzenetetracarboxylic acid).²² The BTC compound contains indium atoms 7-coordinated by the oxygen atoms from two chelating and two bridging carboxylate groups and from a water molecule. In the tetracarboxylate compound, the indium atoms form hydroxide-bridged octahedral chains similar to those in compound **0**. One other mode of indium coordination that has been reported is based on trimers containing three octahedra sharing one central μ^3 -oxo anion, for example, [InO₃H₂O] in [In₃O(C₁₆N₂O₈H₆)_{1.5}(H₂O)₃](H₂O)₃(NO₃).²³ Similar trimeric units are found in In₁₂O(OH)₁₂{OH}₄{H₂O}₅[BTC]₆~31H₂O, which also contains layers comprising groups of three trans-connected indium oxygen octahedra that are each cis-connected to four other trimers.²⁴

Finally, we note that the characterization of the modes of oxide and hydroxide ion coordination to indium(III) presented here may have relevance to studies of the kinetics of ligand binding and hydrolysis of In(III) in aqueous solution.^{25,26}

Acknowledgment. We thank the R. A. Welch Foundation for support of this work.

Supporting Information Available: X-ray crystallographic data, in CIF format, for the structure determinations of **1**–**3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC701126T

- (18) Wang, Y.-L.; Liu, Q.-Y.; Zhong, S.-L. *Acta Crystallogr., Sect. C* **2006**, *62*, m395–m397.
 (19) Sun, J.; Weng, L.; Zhou, Y.; Chen, J.; Chen, Z.; Liu, Z.; Zhao, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 4471–4473.
 (20) Gomez-Lor, B.; Gutierrez-Puebla, E.; Iglesias, M.; Monge, M. A.; Ruiz-Valero, C.; Snejko, N. *Chem. Mater.* **2005**, *17*, 2568–2573.
 (21) Gomez-Lor, B.; Gutierrez-Puebla, E.; Iglesias, M.; Monge, M. A.; Ruiz-Valero, C.; Snejko, N. *Inorg. Chem.* **2002**, *41*, 2429–2432.

- (22) Lin, Z.-Z.; Jiang, F.-L.; Chen, L.; Yuan, D.-Q.; Zhou, Y.-F.; Hong, M.-C. *Eur. J. Inorg. Chem.* **2005**, 77.
 (23) Liu, Y.; Eubank, J. F.; Cairns, A. J.; Eckert, J.; Kravtsov, V. Ch.; Luecke, R.; Eddaoudi, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3278.
 (24) Volkringer, C.; Loiseau, T. *Mater. Res. Bull.* **2006**, *41*, 948.
 (25) Eyring, E. M.; Owen, J. D. *J. Phys. Chem.* **1970**, *74*, 1825.
 (26) Ricciu, A.; Secco, F.; Venturini, M.; García, B.; Leal, J. M. *Chem.—Eur. J.* **2001**, *7*, 4613.