

# In(OH)BDC·0.75BDCH<sub>2</sub> (BDC = Benzenedicarboxylate), a Hybrid Inorganic–Organic Vernier Structure

Ekaterina V. Anokhina, Marie Vougo-Zanda, Xiqu Wang, and Allan J. Jacobson\*

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

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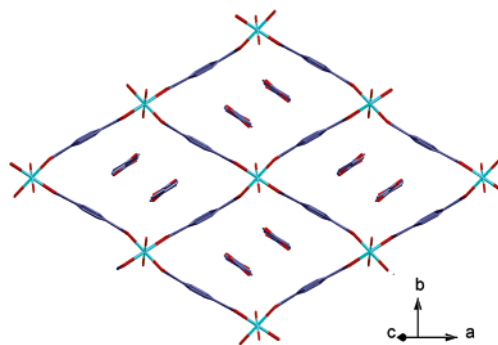
Crystal structures that are composed of two independent sublattices with different periodicities are known as composite, “vernier” or chimney and ladder structures. The superstructure that results from the mismatch in the repeat distances can be a simple rational multiple of the basic unit cell in the commensurate or lock-in state or in the incommensurate state the ratio of the superlattice repeat distance to the basic lattice repeat distance is irrational. Many examples of structures of this type are known, including anion excess fluorites, the Nowotny chimney ladder phases, layered cuprates, and transition metal sulfides and oxides.<sup>1</sup> Vernier structures are also well-known in organic systems such as urea and thiourea inclusion compounds, polymers, and synthetic metals.<sup>2</sup> While several structures show the coexistence of coordination polymer and noncovalent nets via parallel interpenetration,<sup>3</sup> the new compound reported here, In(OH)BDC·0.75BDCH<sub>2</sub> (BDC = benzenedicarboxylate), is to our knowledge the first example of a hybrid inorganic coordination polymer–organic vernier structure; the two sublattices are formed by a covalently linked In(OH)BDC lattice and ordered chains of hydrogen-bonded H<sub>2</sub>BDC molecules.

Férey and co-workers in a series of articles have described the synthesis of the M(OH)BDC phases where M = Al, V, and Cr. All of the compounds with the exception of V(OH)BDC were obtained in polycrystalline form.<sup>4</sup> We have extended the class to include single-crystal growth of Fe(OH)BDC·pyridine, Fe(DMF)-BDC, [Fe<sub>0.28</sub>V<sub>0.72</sub>OH<sub>0.8</sub>(NH<sub>4</sub>)<sub>0.2</sub>(BDC)]·0.53(BDC),<sup>5</sup> and now the indium phase.

In the structure of M(OH)(BDC)·0.7(BDC), the M<sup>3+</sup> cation is coordinated to six oxygen atoms in distorted octahedral geometry and the octahedral M–O centers are linked by sharing *trans*-hydroxyl groups forming bent M–OH–M chains. The oxygen atoms of the BDC groups occupy the equatorial positions of the octahedra. The BDC ligands bridge the chains to form a three-dimensional framework with large diamond-shaped channels.

As synthesized, the channels are filled with H<sub>2</sub>BDC guest molecules which have been reported to be disordered. The guest molecules can be removed by heating at 380–400 °C and other guests can be inserted, for example, water molecules. The replacement of H<sub>2</sub>BDC by water produces a remarkable change in the channel dimensions indicating the flexibility of the framework. Férey and co-workers described the flexibility as “breathing” in response to the size and bonding characteristics of the guest species.<sup>4</sup>

In this communication, we report the synthesis and structure of the new compound In(OH)BDC·0.75H<sub>2</sub>BDC **1** in single-crystal form. Several other indium compounds with BDC ligands have been reported previously. For example, in InH(BDC)<sub>2</sub>,<sup>6</sup> the indium atoms are eight-coordinated by oxygen atoms from three chelating carboxylates, whereas in In<sub>2</sub>(OH)<sub>3</sub>(BDC)<sub>1.5</sub>,<sup>7</sup> the In atoms are six-coordinated by three  $\mu_2$ -hydroxide ions and three different carboxylate ligands. In the related compounds In(BDC)<sub>1.5</sub>(bipyridine) and In<sub>2</sub>(OH)<sub>2</sub>(BDC)<sub>2</sub>(*o*-phenanthroline)<sub>2</sub>, the indium ions are coordinated by two nitrogen atoms and six and four oxygen atoms,



**Figure 1.** View of the structure of **1** showing the orientation of the guest H<sub>2</sub>BDC molecules within the In(OH)BDC framework.

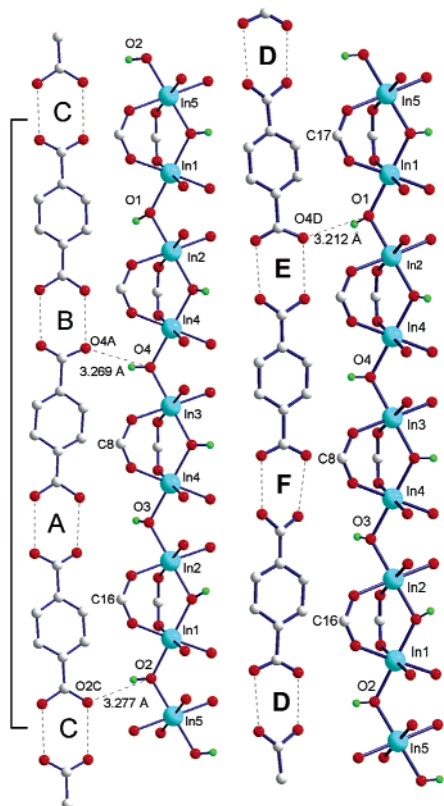
respectively.<sup>8</sup> The six but not the eight-coordinate systems show catalytic activity.

In a typical synthesis of **1**, indium (0.114 g, 1 mmol), 1,4-benzene dicarboxylic acid (0.332 g, 2 mmol), HF (48%, Merck, 0.06 mL), and deionized water (10 mL) in the molar ratios of 1:2:1.5:560 were placed in a hydrothermal reaction vessel and heated at 220 °C for 3 days. After cooling at a rate of 0.5 °C/min to ambient, the product was filtered, washed with DMF to dissolve unreacted H<sub>2</sub>BDC, and dried at room temperature. The final product was a single phase containing single crystals of **1**. The final solution pH was ~1.5.

Thermal decomposition of **1** shows the loss of the H<sub>2</sub>BDC molecules in two clearly separated steps. The weight loss in the temperature range of 200–350 °C corresponds to the removal of half (0.375 mol) of the free H<sub>2</sub>BDC molecules in the channels (14.32% measured, 14.81% calculated). The second weight loss between 350 and 500 °C corresponds to the loss of the remaining 0.375 mol of free H<sub>2</sub>BDC molecules along with 1 mol of framework BDC molecules (52.10% measured, 53.83% calculated).<sup>9</sup> Elemental analysis of a powder sample also gives an H<sub>2</sub>BDC content of 0.74, in agreement with the X-ray data.<sup>10</sup>

The 3D framework of [In(OH)BDC]<sub>4</sub>[H<sub>2</sub>BDC]<sub>3</sub> **1** is closely similar to that of the previously reported M(OH)BDC compounds (Figure 1). In **1**, there are five independent indium oxygen octahedra that are all slightly compressed with axial In–O bond lengths of 2.077(3)–2.084(3) Å and equatorial In–O bond lengths of 2.133(4)–2.154(3) Å.

The axial oxygen atom corners are shared by neighboring octahedra to form a zigzag ...OH–In–OH–In... backbone with In–OH–In angles of 118.6(2)–120.6(2)°. The equatorial oxygen atoms are shared with the BDC anions that cross-link the octahedral chains into a 3D framework. The framework has a channel system filled by guest H<sub>2</sub>BDC molecules that are bound to the framework through relatively weak hydrogen bonds and  $\pi$ – $\pi$  interactions. The guest H<sub>2</sub>BDC molecules are interconnected to form infinite columns through fairly strong hydrogen bonds (OH...O: 2.5–2.7 Å). The framework and the guest H<sub>2</sub>BDC may be considered as two



**Figure 2.** Two columns of H<sub>2</sub>BDC guest molecules in **1**. Guests form hydrogen-bonded chains with O...O distances: A 2.665, 2.564 Å; B 2.608, 2.687 Å; C 2.608, 2.652 Å; D 2.725, 2.560 Å; E 2.625, 2.731 Å; F 2.629, 2.761 Å. The solid line shows the BDC repeat unit.

sublattices. Each InO<sub>6</sub> octahedron of the octahedral chain has a length of 3.6 Å along the chain axis, whereas each H<sub>2</sub>BDC molecule has a length of 9.6 Å along the guest acid column axis. Therefore, a unit of eight InO<sub>6</sub> octahedra of the octahedral chain is just in registry with three H<sub>2</sub>BDC molecules of the guest column, giving a lattice parameter  $c(\sin \beta) = 28.76$  Å, the repeat unit along the channel axis direction [101]. Since there are two guest acid columns for each octahedral chain, there is  $3/4$  H<sub>2</sub>BDC guest molecule for each framework indium atom.

The columns of the H<sub>2</sub>BDC guest molecules were found disordered among two positions related by a translation of  $\sim 2.5$  Å along the column axis. The occupancies of the two positions were refined to (ABC)/(DEF) = 0.812(4)/0.188. Two (A and C) of the three H<sub>2</sub>BDC molecules in column ABC form weak hydrogen bonds to the OH groups of the octahedral chain (Figure 2), which causes slight rotation of the H<sub>2</sub>BDC molecules. The same two H<sub>2</sub>BDC molecules also have weak  $\pi$ - $\pi$  interactions with the framework BDC marked with C8 and C16 in Figure 2. The remaining H<sub>2</sub>BDC molecule B has neither hydrogen bond nor  $\pi$ - $\pi$  interactions with the framework and is well-aligned parallel to the column axis. The guest column DEF is less well-defined because of the low occupancy. Both the intermolecular hydrogen bonds and the interactions with the framework of the column DEF seem weaker than those of column ABC (Figure 2).

The In-OH-In angles in **1** are considerably smaller than the corresponding angle of 124.5° in the Fe<sup>3+</sup> analogue Fe(OH)BDC·

0.85py where the guest molecules are pyridine. This slight constriction of the In-OH-In backbone may be necessary to match the guest acid columns. In the Cr-analogue Cr(OH)BDC·0.75H<sub>2</sub>BDC, the Cr-OH-Cr angle is 121.5° for the as-synthesized phase but increases to 124.8° when the guest H<sub>2</sub>BDC was replaced by H<sub>2</sub>O. Given the slight flexibility of the octahedral chains, we anticipate commensurate vernier structures for other members of this structural family with guest H<sub>2</sub>BDC molecules. Most of the reported structures of these compounds were solved from powder X-ray data that are not accurate enough to reveal the ordered superstructures. Preliminary results on single crystals of Al(OH)BDC0.7H<sub>2</sub>BDC indicate that this is also a vernier compound but with a much larger superstructure.

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**Supporting Information Available:** Synthesis details, tga data, IR spectra, crystal data (CIF format), and details of structure solution and refinement. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) The decomposition behavior was determined by heating in air at 1 °C/min using a TA instruments thermogravimetric analyzer. The infrared spectra of **1** as synthesized and of a sample heated at 320 °C show, in both cases, characteristic stretching vibration bands of the OH group at  $\sim 3600$  cm<sup>-1</sup> and a strong band at approximately 1700 cm<sup>-1</sup>, which is characteristic of free C=O species confirming the presence of free H<sub>2</sub>BDC molecules inside the channels.
- (10) Elemental analyses results: In, 26.76% obsd (27.30% calcd); C, 39.73% obsd (39.98% calcd); H, 2.39% obsd (2.28% calcd). Crystal data: formula, Mr =, space group *P2<sub>1</sub>/c*, *a* = 18.228(3), *b* = 11.970(2), *c* = 34.062(6) Å,  $\beta$  = 122.4(1)°, *V* = 6278(2) Å<sup>3</sup>, *Z* = 4, *T* = 293, *d*<sub>calc</sub> = 1.780 g cm<sup>-3</sup>,  $\mu$ (Mo K $\alpha$ ) = 1.544 mm<sup>-1</sup>. Single-crystal data were collected on a Siemens SMART/CCD diffractometer (38 460 reflections total, 14 686 unique, *R*<sub>int</sub> = 0.0305). An absorption correction was made by using the SADABS program. The structure was solved and refined with the SHELXTL software package. Final refinements converged at *R*<sub>1</sub> = 0.0386 and *wR*<sub>2</sub> = 0.1018 for 6106 reflections with *I* > 2 $\sigma$ (*I*) and *R*<sub>1</sub> = 0.0933 and *wR*<sub>2</sub> = 0.1248 for all 14 686 reflections and 956 parameters. The hydrogen atoms were refined with geometric constraints. Some guest H<sub>2</sub>BDC molecules were refined as rigid groups. The structure has pronounced orthorhombic pseudo symmetry.

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