Novel 2D and 3D Indium Metal-Organic Frameworks: Topology and Catalytic Properties[†]

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Four novel metal-organic frameworks (MOFs) [In(BDC)$_{1.5}$(bipy)] (**1**), [In$_2$(OH)$_2$(BDC)$_2$(phen)$_2$] (**2**), [In(BTC)(H$_2$O)(bipy)] (**3**), and [In(BTC)(H$_2$O)(phen)] (**4**) (BDC = 1,4-benzendicarboxylic acid, BTC = 1,3,5-benzenetricarboxylic acid, bipy = 2,2′-bipyridyl, phen = *o*-phenantroline) were synthesized and their structures were determined by X-ray single-crystal diffraction. Structurally speaking we can conclude that while the metal/connector/chelate rate is 1:1:1, the introduction of a chelate ligand, such as bipy or phen, blocks the possibility of connections in one direction, inducting the formation of 2D structures. In the case of compound **1**, the extra one-half of BDC ligand per indium favors the eight coordination of the metal and drives the formation of a catenated 3D structure. Topological studies on the four compounds show one inclined catenation of hexagonal layers for **1** and three interdigitated layered structures with 2D topologies of type (4⁴), (6³), and (4.8²) for **2**, **3**, and **4** compounds, respectively. Three of the new In compounds are active and selective acid catalyst in acetalization of aldehydes.

Introduction

Reduction in negative environmental impact, which is usually caused by the chemical industry, presents nowadays a mayor scientific challenge. One possible search for a cleaner chemical process is new selective catalysts because improved catalysts can decrease the number of stages in a given process and hence diminish its impact on the environment. In terms of a so-called "green chemistry approach", it seems still more important to design catalysts that can be reused and recycled easily. In this sense, it is very understandable that there currently is considerable interest in metal-organic polymeric materials inspired by their intriguing structural diversity and potential functions as microporous solids for molecular adsorptions, ion exchange, and heterogeneous catalysis.[1−12] In this sense, it is worth mentioning

Janiak's review[13] on coordination polymers applications. From the reported studies, benzene multicarboxylate ligands have been found to be useful building blocks in construction of organic−inorganic materials with desired topologies owing to their rich coordination modes. Particularly, in our previous studies[14] on the indium complex with 1,4-benzendicarboxylic acid, the obtained metal-organic framework (MOF) In$_2$(OH)$_3$-(BDC)$_{1.5}$ has proven to possess interesting catalytic properties in hydrogenation of nitroaromatics and oxidation of sulfide reactions. On the other hand, some additional ligands can modify structure and properties of the resulting compounds, and it is clear that the catalytic activity of MOF would strongly depend on the nature of both the linking carboxylate ligand and metal ion as well as additional ligands present in the structure. *o*-Phenanthroline (phen) and 2,2′-bipyridyl (bipy) proved to be extremely important ligands for metals, and the obtained metal complexes often show attractive chemical and physical properties. While this manuscript was being revised, a new structure of In coordination polymer with BTC ligand appeared.[15] Herein, we report the synthesis and crystal structure of four new polymeric indium mixed ligand complexes constructed from the assembly reaction of the In(III) ion and benzendi- and benzentri-carboxylic acids (1,4-benzendicarboxylic acid, H$_2$BDC and 1,3,5-benzentri-carboxylic, H$_3$BTC) in the presence of additional ligands bipy and phen. Catalytic activity of the new MOFs has been evaluated as well.

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Table 1. Crystal Data and Structure Refinement for 1−4

	1	2	3	4
chemical formula	In(BDC)$_{1.5}$(bipy)	In$_2$(OH)$_2$(BDC)$_2$(phen)$_2$	In(H$_2$O)(BTC)(bipy)·(H$_2$O)$_{0.25}$	In(H$_2$O)(BTC)(phen)
	C$_{22}$H$_{14}$InN$_2$O$_6$	C$_{40}$H$_{26}$In$_2$N$_4$O$_{10}$	C$_{19}$H$_{13.5}$InN$_2$O$_{7.25}$	C$_{21}$H$_{13}$InN$_2$O$_7$
fw	517.17	952.28	500.62	520.15
temp	296(2) K	296(2) K	296(2) K	296(2) K
cryst syst	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	*Pbca*	*P*2$_1$/*n*	*Pbca*	*P*2$_1$/*n*
unit cell dimensions	$a = 13.490(2)$	$a = 13.1446(6)$	$a = 14.260(6)$	$a = 7.8171(7)$
	$b = 16.202(2)$	$b = 15.4921(8)$	$b = 14.184(6)$	$b = 13.4926(12)$
	$c = 17.065(2)$	$c = 17.2293(8)$	$c = 18.653(8)$	$c = 17.3708(2)$
		$\beta = 100.469(10)$		$\beta = 96.545(2)$
V (Å^3); Z	3729.9(8); 8	3450.1(3); 4	3773(3); 8	1820.2; 4
D_x (Mg m^{-3})	1.842	1.831	1.754	1.898
absorption coefficient	1.314 mm^{-1}	1.407 mm^{-1}	1.300 mm^{-1}	1.351 mm^{-1}
$F(000)$	2056	1884	1968	1032
cryst size, mm	0.20 × 0.25 × 0.30	0.30 × 0.20 × 0.10	0.16 × 0.20 × 0.25	0.10 × 0.20 × 0.20
data collection θ range	3.78−31.36°	3.81−31.29°	3.20−23.26°	3.36−30.90°
limiting indices	$-18 \leq h \leq 19$	$-14 \leq h \leq 19$	$-12 \leq h \leq 15$	$-10 \leq h \leq 11$
	$-23 \leq k \leq 23$	$-22 \leq k \leq 21$	$-15 \leq k \leq 15$	$-19 \leq k \leq 16$
	$-24 \leq l \leq 14$	$-23 \leq l \leq 24$	$-20 \leq l \leq 20$	$-24 \leq l \leq 23$
reflns collected	22851	22860	12447	11557
independent reflns	5617	9710	2681	4967
	($R_{int} = 0.1088$)	($R_{int} = 0.0741$)	($R_{int} = 0.1029$)	($R_{int} = 0.0813$)
GOF on F^2	0.89	0.87	1.10	0.81
final R indices [$I > 2\sigma(I)$]	R1 = 0.045,	R1 = 0.039,	R1 = 0.065,	R1 = 0.038,
	wR2 = 0.071	wR2 = 0.074	wR2 = 0.131	wR2 = 0.06
W scheme coeff.	0.0245, 0.00	0.0462, 0.00	0.0705, 0.00	0.0107, 0.00
largest diff. peak and hole, e Å^{-3}	0.62 and −1.16	0.59 and −1.04	1.32 and −1.24	0.63 and −0.86

Experimental Section

General Information. All commercially available (Aldrich) products were used without further purification [InCl$_3$ (98%), 1,4-benzendicarboxylic acid (H$_2$BDC) (98%), 1,3,5-benzenetricarboxylic acid (H$_3$BTC) (99%), 2,2′-bipyridyl (bipy) (99%), 1,10-phenantroline (phen) (98%), and triethylamine (99%)]. The IR spectrum was recorded from KBr pellets in the range 4000−400 cm^{-1} on a Perkin-Elmer spectrometer. Thermogravimetric and differential thermal analyses (TGA-DTA) were performed using a SEIKO TG/DTA 320 apparatus in the temperature range between 25 and 700 °C in a N$_2$ (flow of 50 mL/min) atmosphere and at a heating rate of 5 °C/min.

Synthesis. *[In(BDC)$_{1.5}$(bipy)] (1).* Compound **1** was obtained by the hydrothermal reaction of InCl$_3$ (0.56 g, 2.53 mmol), H$_2$BDC (0.84−1.68 g, 5.06−10.12 mmol), bipy (0.511−1.022 g, 5.06−10.12 mmol), and 25 mL of water (the solution was adjusted to pH = 6 by the addition of triethylamine, an approximate amount of 0.5 mL) in a 43-mL stainless steel bomb with a Teflon liner at 170 °C for 48 h. After cooling slowly at room temperature, the colorless obtained crystals were filtered and washed thoroughly with deionized water and ethanol and dried in air (yield 55% based on In). Anal. Calcd for C$_{22}$H$_{14}$InN$_2$O$_6$: C, 51.05; H, 2.71; N, 5.41. Found: C, 51.22; H, 2.91; N, 5.00. The rate of purity of each product was tested also by comparison of the XRD powder patterns of the bulk products with those simulated with atomic coordinates derived from single-crystal X-ray diffraction.

[In$_2$(OH)$_2$(BDC)$_2$(phen)$_2$] (2). This complex was prepared similarly to **1** with the exception that bipy was replaced by phen. Pale yellow crystals of **2** were obtained after hydrothermal treatment at 170 °C (yield 66% based on In). Anal. Calcd for C$_{40}$H$_{26}$In$_2$N$_4$O$_{10}$: C, 50.41; H, 2.73; N, 5.88. Found: C, 50.78; H, 2.21; N, 5.82.

[In(BTC)(H$_2$O)(bipy)] (3). The compound was prepared similarly to **1** with the exception that H$_2$BDC was replaced by H$_3$BTC. The hydrothermal synthesis was carried out for 48 h at 170 °C (yield 65% based on In). Anal. Calcd for C$_{19}$H$_{13}$InN$_2$O$_7$: C, 45.95; H, 2.62; N, 5.64. Found: C, 45.62; H, 2.11; N, 6.04.

[In(BTC)(H$_2$O)(phen)] (4). This compound was prepared similarly to **2** with the exception that H$_2$BDC was replaced by H$_3$BTC (yield 62% based on In). Anal. Calcd for C$_{21}$H$_{13}$InN$_2$O$_7$: C, 48.45; H, 2.50; N, 5.38. Found: C, 48.28; H, 2.14; N, 5.72.

X-ray Structure Determination. A summary of the main crystal and refinement data for the four compounds is given in Table 1. Data for single crystals of **1−4** were collected in a Siemens SMART CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation = 0.71073). Data were collected over a hemisphere of the reciprocal space by a combination of three sets of exposures. Each exposure of 20 s covered 0.3° in ω. Unit cell dimensions were determined by a least-squares fit of 60 reflections with $I > 20\sigma(I)$. Data were collected using ω scan over the range 3°< θ < 26°. Spectra were quite poor at high angles, specially those of compounds **1** and **4** as can be seen in their R_{int} values (Table 1). This fact drives to R_w values smaller than R when using all reflections for these two compounds. No absorption correction was applied. The structures were solved by direct methods. The final cycles of refinement were carried out by full-matrix least-squares analyses with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were situated at their calculated positions, except for those involved in coordinated water molecules and hydroxyl groups, which were located by Fourier difference synthesis and isotropically refined. Calculations were carried out with SMART software for data collection and data reduction and SHELXTL.[16]

Catalytic Experiments. Activation of the catalysts was performed by heating the solids at 100 °C for 12 h. After this time, solutions of the carbonyl compound (2.54 mmol) and TMOF (1.30 mmol) in tetrachloromethane (3 mL) were added onto the activated catalysts. The resulting suspensions were magnetically stirred at reflux temperature for 3.5 h. Samples were taken from each reaction at intervals and the reaction products were analyzed by gas chromatography.

Results and Discussion

X-ray single-crystal studies on the samples obtained from the four indicated reactions revealed their compositions: **In-**

(16) *Software for the SMART System V5.04 and SHELXTL V 5.1*; Bruker-Siemens Analytical X-ray Instrument Inc.: Madison, WI, 1998.

1: In(BDC)₁.₅(bipy)   **2: In₂(BDC)₂(OH)₂ (phen)₂**   **3: In(BTC)(H2O)(bipy)**   **4: In (BTC)(H2O)(phen)**
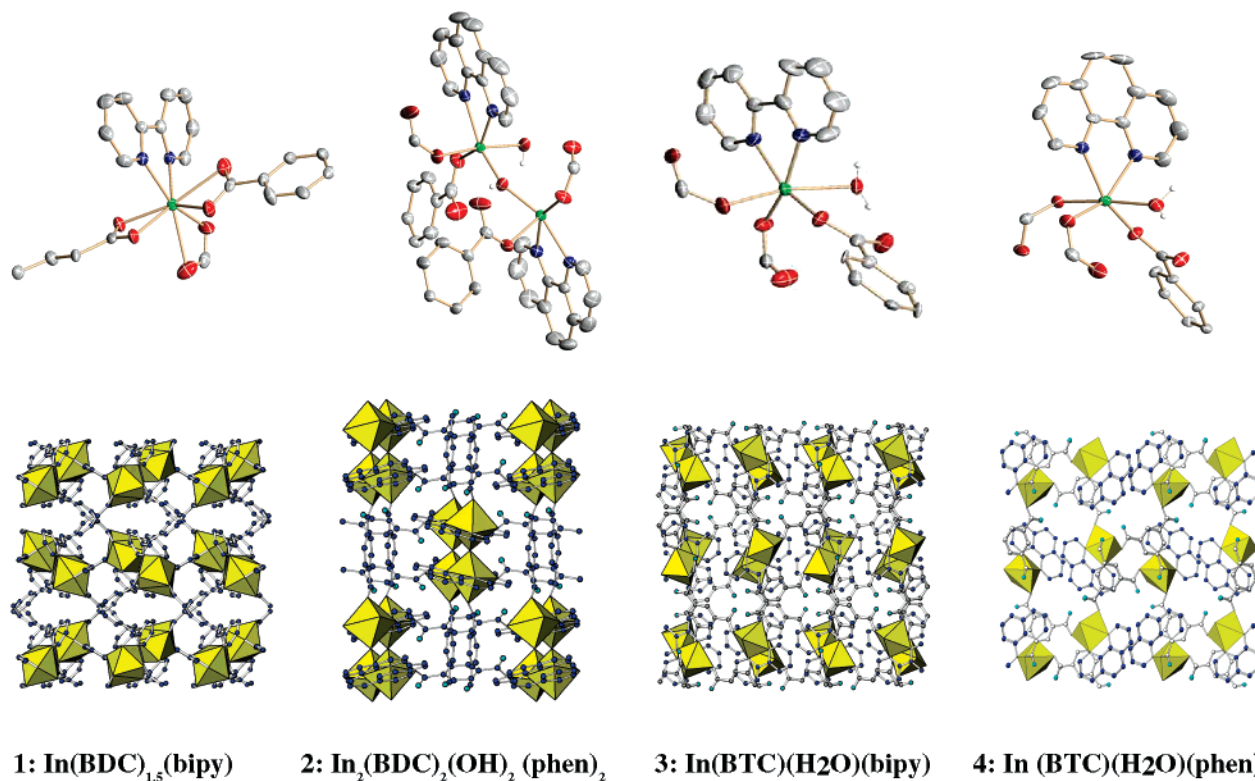
Figure 1. (Top) ORTEP drawing with ellipsoids probability 50%. Red ellipsoids, O; green, In; blue, N; gray, C. (Bottom) View of structures showing the In polyhedra in yellow for compounds **1−4**.

Table 2. Indium Coordination Bond Distances (Å) for Compounds 1−4

	compound						
1		**2**		**3**		**4**	
In(1)−O(1)	2.552(4)	In(1)−O(1)	2.105(3)	In(1)−O(1)	2.111(6)	In(1)−O(1)	2.121(2)
In(1)−O(2)	2.204(3)	In(1)−O(2)	2.127(3)	In(1)−O(2)	2.093(6)	In(1)−O(3)	2.123(3)
In(1)−O(3)	2.221(3)	In(1)−O(4)	2.195(2)	In(1)−O(3)	2.133(6)	In(1)−O(5)	2.141(2)
In(1)−O(4)	2.453(3)	In(1)−O(10)	2.118(3)	In(1)−O(4)	2.223(6)	In(1)−O(7)	2.193(3)
In(1)−O(5)	2.278(3)	In(1)−N(1)	2.293(3)	In(1)−N(1)	2.281(8)	In(1)−N(1)	2.306(3)
In(1)−O(6)	2.303(3)	In(1)−N(2)	2.345(3)	In(1)−N(2)	2.268(8)	In(1)−N(2)	2.302(3)
In(1)−N(1)	2.348(3)	In(2)−O(1)	2.132(3)				
In(1)−N(2)	2.295(3)	In(2)−O(7)	2.111(3)				
		In(2)−O(8)	2.127(3)				
		In(2)−O(10)	2.116(3)				
		In(2)−N(3)	2.326(3)				
		In(2)−N(4)	2.336(3)				

(BDC)₁.₅(bipy) (1), In₂(BDC)₂(OH)₂(phen)₂ (2), In (BTC)-(H₂O)(bipy) (3), and In(BTC)(H₂O)(phen) (4). Main data collection and refinement details are in Table 1. Figure 1 shows the asymmetric units, and Table 2 summarizes the coordination bond lengths for the four compounds.

The structure of **1** consists of a three-dimensional entanglement formed by catenation of bidimensional hexagonal layers, in which every In³⁺ ion is connected to three bidentate chelating carboxylate groups of three different fully deprotonated bridging (BDC)²⁻ units. Each In³⁺ ion is further bidentately coordinated to two nitrogen atoms of one bipy molecule to form eight-coordinate metal ions. The asymmetric unit consists, thus, of one In center, 1.5 bridging 1,4-benzendicarboxylic anions, and one bipy molecule (Figure 1). The carboxylic O−In bond distances range from 2.204-(3) to 2.551(4) Å and those of the bipy's N−In bonds from 2.295(3) to 2.349(3) Å, all of which are comparable to those usually encountered for indium−oxygen and indium−nitrogen coordination.[17,18] Worth mentioning here is that this is the only compound, among the four under consideration

in this paper, where the carboxylate groups are chelating bidentate. This compound presents a rare example of eight-coordinated indium cation.[19] Regarding the structure, two different roles are played by the connectors (BDC): one of them L, situated in the general position, is joining the In atoms along the *b* direction to give 1D $[In(bipy)(L)]_{\infty}^{+}$ infinite zigzag chains. The other BDC molecule L′, whose centroid is situated on an inversion center, keeps these chains bonded along the [1 0 0] direction, giving rise to (6,3) hexagonal layer of formula [In(bipy)(L−L)′]. Two identical sets of parallel hexagonal layers, spanning two different stacking directions, are interlocked in "inclined" mode, giving an overall 3D entangled architecture (see Figure 2). Each 6-ring is interlocked with two distinct inclined layers [Doc = *(2/2)*].[20]

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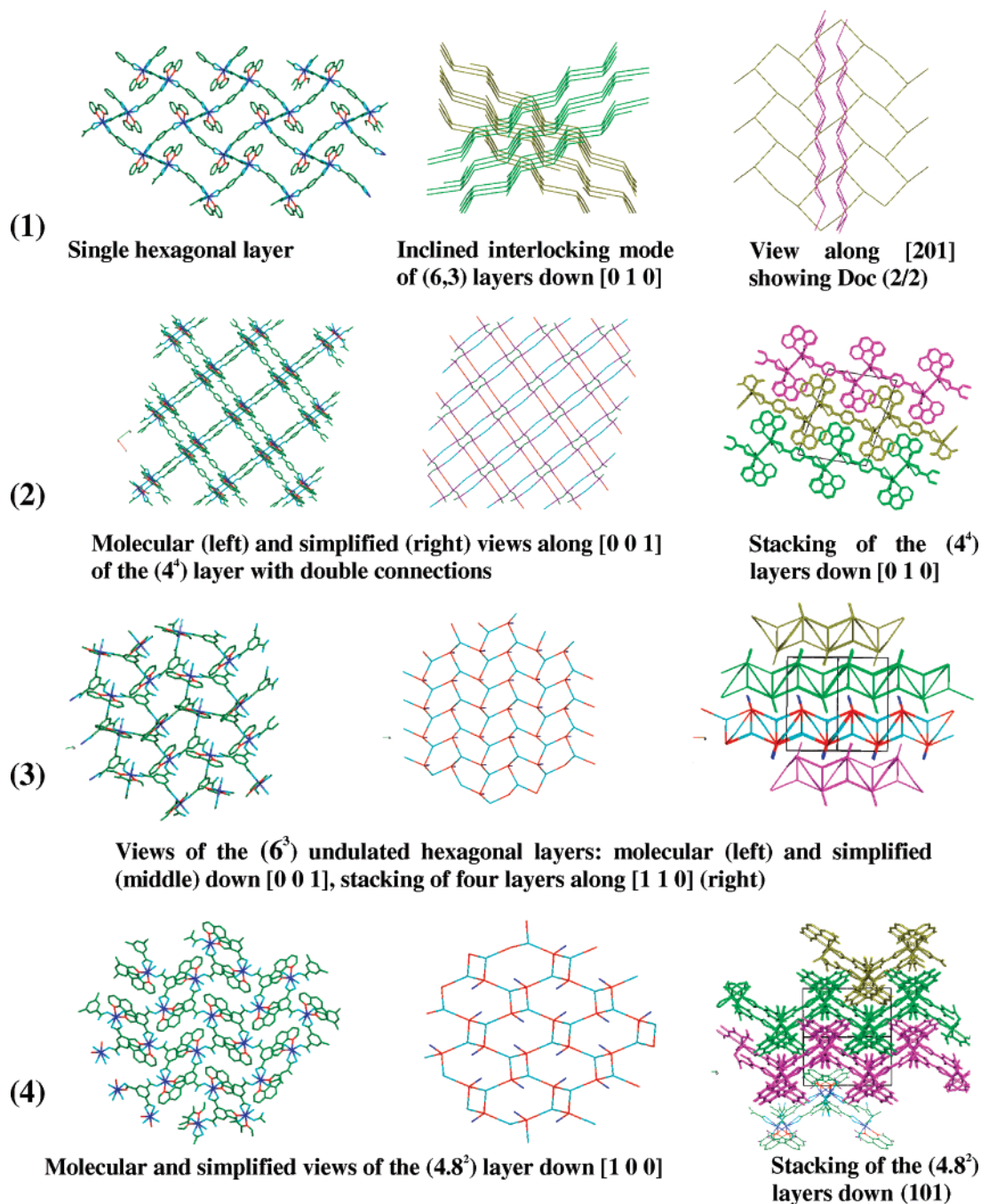(19) Preut, H.; Huber, F. Z. *Anorg. Allg. Chem.* **1979**, *450*, 12.

Novel 2D and 3D Indium Metal-Organic Frameworks

Chem. Mater., Vol. 17, No. 10, 2005 **2571**

Figure 2. Topological study on compounds **1**–**4**.

In compound **2**, the local coordination geometry around each indium atom can be described as slightly distorted octahedra formed by two μ_2-OH groups, two oxygen atoms from different carboxylates of BDC, and two nitrogen atoms of phen (Figure 1). The μ_2-OH groups join four In atoms to give tetrameric $[In_4(OH)_4(phen)_4]^{8+}$ units. The (BDC) connectors link the tetramers along the *a* and *b* directions, giving rise to infinite layers perpendicular to the (001) direction of composition $[In(BDC)(OH)(phen)]_\infty$. The topological study of this structure shows a new 2D layer of square type (4^4) with "double" connections.[20] Each side of the square is doubled, which makes a 4^4 topology just with squares and rectangles. The square layers stack along the [010] direction

with the phenantroline molecules pointing toward the interlamellar space in an interdigitated way (Figure 2).

In compounds **3** and **4**, indium ions are six-coordinated to two nitrogen atoms of one bipy or phen molecule, to three oxygen atoms of three carboxylate groups from different bridging (BTC) connectors, and to one water molecule. Distances and angles involving In atoms coordination are also similar. Despite being different crystal systems (orthorhombic and monoclinic, correspondingly), certain similitude is also found in their polymeric packing. In both compounds each (BTC) connector links monodentately three In atoms, leaving, thus, three uncoordinated oxygen atoms (Figure 1). This arrangement gives rise to layers perpendicular to the [001] and [100] directions for **3** and **4**, respectively. These two compounds have the same stoichiometry, with the only

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difference of the chelating ligand (bipy vs phen). Their packing is built by interdigitated parallel layers. The topology[20] of the layers being (6^3) and (4.8^2) for **3** and **4** compounds, respectively, makes the difference between both structures (see Figure 2). Topological study for the four compounds was done with TOPOS.[21]

Structurally speaking, we can conclude that while the metal/connector/chelate rate is 1:1:1, the introduction of a chelate ligand, such as bipy or phen, blocks the possibility of connections in one direction, inducting the formation of 2D structures. In the case of compound **1**, as indicated above, this proportion is 1:1.5:1. The extra one-half of connector drives the formation of the catenated 3D structure. Besides, the geometrical features of the BTC ligand seems to be the cause of the incorporation of a water molecule in a coordination position for **3** and **4** compounds, while the linearity of the BDC ligand allows either the eight coordination for the indium, acting as chelate, or the formation of tetrametallic clusters in compounds **1** and **2**, respectively.

All the IR spectra of the compounds **1**−**4** are quite similar. There are no absorption bands in the area 1710−1675 cm^{-1}, which proves the complete deprotonation of the carboxyl groups of the carboxylic acids in the compounds. The characteristic bands of the deprotonated carboxylate groups appear in the region 1640−1550 cm^{-1} for the antisymmetric stretching and 1350−1300 cm^{-1} for the symmetric ones. In the IR spectra of **4** there appears a broad band between 2600 and 3000 cm^{-1}, which corresponds to coordinated water molecules.

The TGA-DTA study has been performed under a nitrogen environment on the as-synthesized products, which had proved to be quite pure according to the elemental analysis and X-ray powder diffraction measurements of **1**−**4**, showing the coincidence with the simulated patterns made on the basis of the single-crystal determinations. The compounds **1** and **2** are stable up to ~350 °C and show a unique sharp decomposition process, with the maximum rate at 440 and 425 °C, correspondingly. The total decomposition of **3** and **4** involves two mass losses. The first steps correspond to a coordinated water molecules loss with the maximum rate at 187 and 295 °C for **3** and **4**, correspondingly. Despite the difference in the temperature of the water molecule losses for **3** and **4**, their frameworks are similar in thermal stability: the second weight loss that corresponds to the total decomposition of **3** and **4** occurs within similar temperature limits with the maximum rate at 440 and 430 °C for **3** and **4**, correspondingly. The total weight losses for **1**−**4** are in agreement with the removal of the organic ligands. PXRD analysis indicated In$_2$O$_3$ (PDF: 760152)[22] as the only residue after the samples of **1**−**4** were heated to 700 °C.

Catalytic Properties. Formation of acetals is one of the most useful protecting methods for carbonyl compounds,[23] and a large amount of synthetic work has been done on the

Table 3. Acetalization of Benzaldehyde with Trimethyl Ortoformate

cat.	t (h)	conv. (%)	TOF (h^{-1})
0	2	68^a	281
1	4	22	75
2	2	56^a	230
3	2	60^a	300
4	2	76^a	380

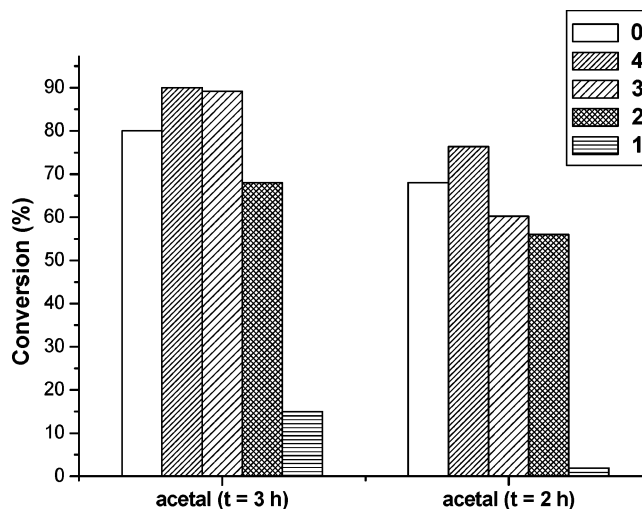^{a} Total conversion was achieved after 6 h.

Figure 3. Yield for In-catalyzed acetalization of benzaldehyde at 2 h.

protection and masking of the carbonyl group. Acetals are important in carbohydrate[24] and steroid chemistry.[25] In the pharmaceutical,[26] phytopharmaceutical, fragrance,[27] and lacquer industries, acetals are used both as intermediates and as final products. The most general method for the synthesis of acetals is to react carbonyl compounds with an alcohol or an ortho ester in the presence of acid catalysts and in this sense *p*-toluensulfonic acid is often used.[28]

The capabilities of the compounds **1**−**4** as catalysts have been tested in acetalization of aldehydes; the results of these tests are collected in Table 3 and Figure 3.

As can be seen, three of the In compounds are active and selective catalysts for acetalization of aldehydes. The reaction of benzaldehyde with trimethyl orthoformate (TMOF) proceeds with high conversion and the corresponding dimethyl acetal is obtained in up to 70% yield (TOF up to 380 as mmol subs./mmol cat. h), in relatively short reaction time (4 h) and under mild conditions (60−70 °C) using the In compounds (10 mol %) as catalysts; in such a way a

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protection of aldehydes by formation of the corresponding dimethyl acetals have been carried out successfully using **In** as acid catalysts except for **1** compound. Two facts distinguish this last compound from the other three; the eight coordination of the In atom and the nonexistence of uncoordinated oxygen atoms. To see which of these two factors is the cause for why it does not act as a catalyst in the tested reactions, we have performed the same reaction for the compound $In_2(OH)_3(BDC)_{1.5}$[11] (compound **0**), in whose structure the In atoms are six-coordinated but none of the oxygen atoms is uncoordinated. As can be seen in Table 3, the catalytic activity of **0** compares very well with our three new catalysts. Consequently, we can conclude that the lack of activity of **1** is due to the hindered accessibility of the reactants to the In active centers because of the eight coordination.

It has to be noticed that while most Lewis acids are decomposed or deactivated in the presence of water, the new Lewis heterogeneous catalysts are stable both in water and organic solvents and can be easily recovered by filtration and reused at least in four cycles without loss of yield or selectivity. After carrying out the complete heterogeneous reaction of aldehydes acetalization, the catalyst was filtered and washed, and then fresh substrate and solvent were added to the recovered catalyst: both activity and reaction yield were found retained for several consecutive experiments. After each of them, filtrate was used in a new reaction and no catalytic activity was found. On the other hand, the solid heterogeneous catalysts were routinely checked by X-ray powder diffraction before and after reactions, showing no alteration.