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In$_2$(OH)$_3$(BDC)$_{1.5}$ (BDC = 1,4-Benzendicarboxylate): An In(III) Supramolecular 3D Framework with Catalytic Activity

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The new hybrid inorganic–organic polymer In$_2$(OH)$_3$[O$_4$C$_8$H$_4$]$_{1.5}$ has been hydrothermally obtained. Conditions for the synthesis are reported. The crystal structure of this material has been established by single-crystal X-ray diffraction: it is monoclinic, with space group $P2_1/c$ (No. 14), $a = 6.772(1)$ Å, $b = 10.329(2)$ Å, $c = 20.152(3)$ Å, $\beta = 97.573(3)°$. The In atoms are octahedrally coordinated by three hydroxide groups and three different molecules of carboxylate ligand. The resulting polymeric 3D structure can be envisaged as having been generated from a honeycomb (6,3) 2D that is cross-linked by the BDC organic anions. Data of IR and TGA-DTA studies, as well as the results of reduction of nitroaromatics and selective oxidation of organic sulfide reactions catalyzed by the new material, are reported.

Introduction

In the past few years, a research area, synthesis and characterization of infinite 1D−3D architectures, designed from metal-based coordination, has been expanded drastically.[1−8] However, the preparation of new types of polymers using crystal engineering continues to be important because of the increase in demand of materials for application in catalysis, separations, and so forth.[9] Hybrid inorganic−organic polymers with zeolite-like frameworks usually have more or less predictable structures and can have a number of advantages over traditional zeolites.[10] A common aproach for the design of such materials is the use of metal centers coordinated to multidentate rigid ligands containing N- or/ and O-donor atoms. The utilization of carboxylates, and, in particular, 1,4-benzendicarboxylate (BDC), has yielded many new noninterpenetrating open frameworks of transition and rare earth metals with variable cavities or channels.[11−13] Organoindium reagents have been used in a variety of transformations[14−18] including allylations, Reformatsky reactions, and cyclopropanations. In the past few years, indium(III) halide complexes have been found to be efficient Lewis acid catalysts[19−21] in reactions such as Mukaiyama aldol reactions, Friedel−Crafts acylations, and Diels−Alder cycloadditions. Besides, indium metal has also been found to be an effective reducing agent.[22−26] Hydrogenation of aromatic nitro compounds with heterogeneous catalysts is often the method of choice for the preparation of the corresponding anilines. Noble metals Pt and Pd supported

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Table 1. Crystal Data and Structure Refinement for $In_2(OH)_3(BDC)_{1.5}$

empirical formula	$In_2(OH)_3(O_4C_8H_4)_{1.5}$
fw	526.8
temp	296(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimensions	$a = 6.772(1)$ Å
	$b = 10.330(2)$ Å; $\beta = 97.573(3)°$
	$c = 20.152(3)$ Å
vol, Z	1397.3(4) $Å^3$, 4
density (calcd)	2.504 Mg m^{-3}
abs coeff	3.348 mm^{-1}
$F(000)$	1004
cryst size	0.08 mm × 0.08 mm × 0.02 mm
Θ range for data collection	3.87°−26.37°
limiting indices	(−8, −12, −23) (8, 12, 25)
reflns collected	6876
independent reflns	2726 ($R_{int} = 0.08$)
abs correction	SADABS
max and min transmission	1.437 and 0.472
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	2726/0/225
GOF on F^2	0.911
final R indices [$I > 2\sigma(I)$]	R1 = 0.051, wR2 = 0.094
R indices (all data)	R1 = 0.099, wR2 = 0.095
largest diff peak and hole	0.841 and −1.239 e $Å^{-3}$

on active carbon are frequently used as catalysts for this reaction.[27] Many of these methods have some drawbacks such as the incompatibility with other functional groups in the molecule. Therefore, new methods for the selective reduction of nitro groups continue to be developed. On the other hand, catalytic oxidation in the liquid phase is widely used in bulk manufacture,[28] becoming increasingly important in the synthesis of fine chemicals, where traditional processes employing inorganic oxidants are under increasing environmental pressure.[29] Herein, the synthesis, crystal structure, and characterization of $In_2(OH)_3(BDC)_{1.5}$ is reported, as well as its potential as a reductant of nitroaromatic substrates and oxidant of organic sulfides.

Experimental Section

General information. All reagents were commercially available ($InCl_3$ 98%, H_2BDC 98%, and triethyl amine 99% Aldrich) and used as received. 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 N_2 (flow of 50 mL min^{-1}) and static air atmosphere and at a heating rate of 5 °C/min.

Synthesis. A mixture of $InCl_3$ (0.56 g, 2.53 mmol), H_2BDC (0.84−1.68 g, 5.06−10.12 mmol), Et_3N (0.511−1.022 g, 5.06−10.12 mmol), and H_2O (25 mL) in a molar ratio 1:(2−4):(2−4):550 was heated in a 43-mL stainless steel reactor with a Teflon liner at 150 °C for 14 h. The colorless obtained crystals were filtered and washed thoroughly with deionized water and ethanol. The solid was purified by heating at 325 °C over half an hour to eliminate the $(Et_3N)H_2BDC$ salt formed. Elemental analysis of the purified material for $C_{12}H_9O_9In_2$ Calcd: C, 27.32; H, 1.52. Found: C, 27.62; H, 1.21.

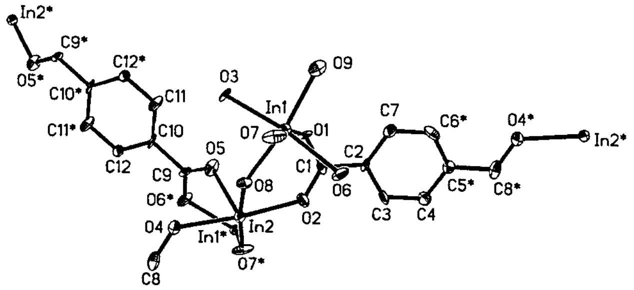

Figure 1. Labeled ORTEP plot of the building unit in the hybrid polymer $In_2(OH)_3(BDC)_{1.5}$ showing more than the asymmetric unit; asterisk indicates atoms that are symmetrically related.

X-ray Structure Determination. Data for a colorless prismatic single crystal of $In_2(OH)_3[O_4C_8H_4]_{1.5}$ were collected in a Siemens SMART-CCD diffractometer, 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 $3° < \theta < 26°$. The total number of reflections measured was 6876 of which 2726 were independent. The structure was solved by direct methods. Refinement was carried out by full-matrix least-squares analysis with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located in a Fourier map and isotropically refined. The final residuals were $R_F = 0.05$ for $I > 2\sigma(I)$ and 0.09 for all data. A summary of the main crystal and refinement data is given in Table 1. Calculations were carried out with SMART software for data collection and data reduction and SHELXTL.[30]

Catalytic Experiments. The catalytic properties of the title compound in hydrogenation reactions of nitroaromatics (nitrobenzene and 2-methyl-1-nitronaphthalene) were examined under conventional conditions for batch reactions in a reactor (Autoclave Engineers) of 100 mL capacity at 313 K temperature, 4 atm dihydrogen pressure, and a metal/substrate molar ratio of 1/1000. The results were monitored by GLC using an internal standard reference. In oxidation of sulfides, the catalyst (5%), acetonitrile as the solvent (1 mL), the substrate (sulfide, 1 mmol), and 30% H_2O_2 (3 mmol) were placed in a 15-mL glass vial. The reaction vessel was heated at a constant temperature with stirring. The reaction mixtures were analyzed by GC, and the reaction products were identified by GC-MS analysis.

Results and Discussion

Single-crystal X-ray diffraction studies on the sample obtained from the reaction product revealed its composition, $In_2(OH)_3(BDC)_{1.5}$, and an extended structure composed of the building units shown in Figure 1. Crystal data and selected bond lengths and angles are presented in Tables 1 and 2. Each of the two independent indium atoms in the asymmetric unit is octahedrally coordinated by three μ2-OH groups and three oxygen atoms from three different BDC ligands. Each oxygen atom of the OH anions is bridging two indium atoms in the structure, these joints giving rise to what can be considered an infinite six-member ring containing sheets of composition $[In_2(OH)_3]_\infty^{3+}$, where each In1 atom is connected to three In2 atoms and vice versa (Figure 2a).

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $In_2(OH)_3(BDC)_{1.5}$[a]

In1−O7	2.058 (7)	In1−O8	2.095 (7)
In1−O9	2.124 (7)	In1−O3	2.156 (6)
In1−O1	2.183 (6)	In1−O6	2.193 (6)
In2−O7^1	2.088 (7)	In2−O8	2.099 (7)
In2−O4	2.164 (6)	In2−O9^2	2.174 (7)
In2−O2	2.192 (6)	In2−O5	2.215 (6)
O7−H7	0.83 (10)	O8−H8	0.79(10)
O9−H9	0.79 (9)		

O7−In1−O8	94.7 (3)	O7^1 −In2−O4	98.2 (3)
O8−In1−O9	165.1(3)	O7^1−In2−O9^2	86.2 (3)
O8−In1−O3	81.3 (3)	O4−In2−O9^2	91.7 (3)
O7−In1−O1	166.0(3)	O8−In2−O2	89.5 (3)
O9−In1−O1	86.5 (3)	O9^2−In2−O2	92.4 (3)
O7−In1−O6	84.0 (3)	O8−In2−O5	95.3 (3)
O9−In1−O6	98.8 (3)	O9^2−In2−O5	170.0 (3)
O1−In1−O6	82.1 (2)	O7^1−In2−O8	173.2 (3)
O7−In1−O9	97.2 (2)	O8−In2−O4	87.7 (3)
O7- In1−O3	94.9 (3)	O8−In2−O9^2	90.4 (3)
O9−In1−O3	88.9 (3)	O7^1−In2−O2	84.8 (3)
O8−In1−O1	84.0 (3)	O4−In2−O2	175.0(2)
O3−In1−O1	98.7 (3)	O7^1−In2−O5	89.0(3)
O8−In1−O6	91.2 (3)	O4−In2−O5	80.3(3)
O3−In1−O6	172.3 (3)	O2−In2−O5	95.8(3)

[a] Symmetry transformations used to generate equivalent atoms: 1 = $(-x + 1, y - 1/2, -z + 1/2)$; 2 = $(x + 1, y, z)$.

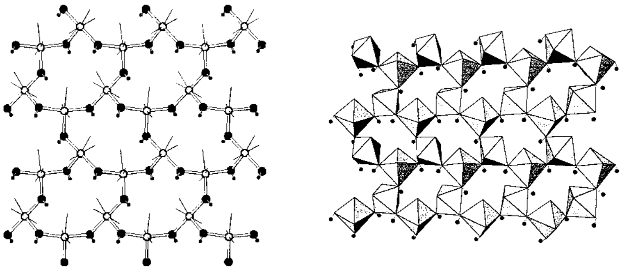

Figure 2. (a) View of the $[In_2(OH)_3]_\infty^{3+}$, (6,3) sheet (single lines show the direction in which octahedra are completed by the oxygen atoms of the BDC). (b) Polyhedral representation of the InO_6 vertex sharing octahedra layer in the new $In_2(OH)_3(BDC)_{1.5}$.

The In−In average distance is 3.77 Å, longer, as expected, but comparable with those of purely inorganic structures, such as the corundum-like In_2O_3 structure[31] or the indium metal (d = 3.34 Å in both cases). The layer is repeated by translation about every 10 Å along the c stacking direction. The $(BDC)^{2-}$ counterions do not act as chelating, but each of them is coordinated to four different indium atoms, (two of each layer) acting as pillars, Figure 3. The two crystallographically independent BDC ligands are situated parallel to the ac plane; two-thirds of them are directed in the [101] and one-third in the [10$\bar{1}$] directions. This disposition that is probably due to the $\pi-\pi$ repulsion of the aromatic rings creates a wall-like perpendicular to the b axis that avoids the formation of channels along this direction and gives rise to two independent organic nets that cross the $[In_2(OH)_3]_\infty^{3+}$ inorganic layers completing the octahedral coordination of the In atoms, Figure 4. The resulting 3D structure can be envisaged as having been generated from a honeycomb (6,3) 2D structure that is cross-linked by the tetratopic BDC spacer link nets.

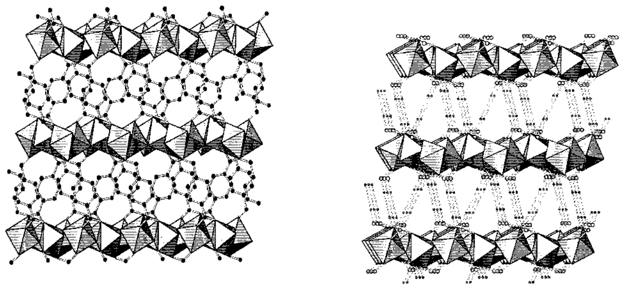

Figure 3. View along the [010] direction of the 3D structure showing the alignement of the aromatic rings along the [101] and [10$\bar{1}$] directions. In the right side, the BDC ligand has been reduced to a line for clarity.

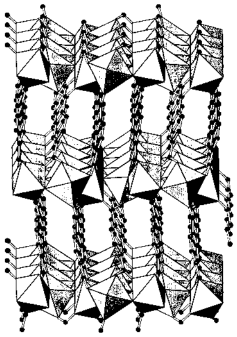

Figure 4. View of the 3D structure of $In_2(OH)_3(BDC)_{1.5}$ along the [100] direction.

If an inorganic layer formed by vertex sharing InO_6 octahedra (three oxygen atoms of OH groups and the other three of BDC ligands) is now considered (Figure 2b), it reminds us in some way of that of the In_2O_3 oxide with corundum structure.[31] This structure could be regarded as built from separated slices of the corundum structure in which because of the geometrical features of the intercalated carboxylate groups, the InO_6 octahedra are not allowed to share edges but vertex.

The IR spectrum of the pure material exhibits a sharp peak in the area 3600 cm^{-1} corresponding to the OH group vibrations. The absence of any strong absorption bands in the area 1710−1675 cm^{-1} confirms the complete deprotonation of the carboxyl groups of the BDC in the compound. The characteristic bands of the dicarboxylate groups appear in the usual region at 1564 and 1536 cm^{-1} for the antisymmetric stretching and at 1392 and 1384 cm^{-1} for the symmetric ones. The separations (Δ) between ν_{asym} (CO_2) and ν_{sym} (CO_2) are 172 and 152, respectively, which agree with the bridging character of the COO^- groups in the compound.[32]

The TGA-DTA study was done on the as-synthesized product. The total decomposition involves two mass losses. A sharp endothermic loss occurs between 230 and 315 °C and corresponds to the decomposition of the salt (Et_3N)-H_2BDC (calcd 26.0%, found 26.3%) present in the crude product because of the excess of BDC. The compound is stable up to 425 °C; the X-ray powder diffraction measurements coincide with the simulated pattern made on the basis of the single crystal determination. The second weight loss corresponds to the decomposition of the material giving

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crystalline In_2O_3 (PDF: 760152).[33] In the second decomposition step, the total mass losses observed and calculated are 54.8% and 52.7%, respectively.

Impurities in the as-synthesized material are readily eliminated. A TGA study performed on the purified material does not show the first weight loss. Remarkably, the structure remains unchanged after heating at 400 °C. This fact that has been also proved by refining the crystal structure in a single crystal after the thermal treatment is important in order to use this material as catalyst.

Catalytic Properties. The capability of $In_2(OH)_3(BDC)_{1.5}$ as catalyst has been tested in hydrogenation of nitroaromatics and oxidation of sulfide reactions. The small size of the pore in this structure avoids the accessibility of the substrates to the metallic centers, the catalytic reactions thus taking place on the surface. Accordingly, the reaction rates are quite similar, not showing any dependence on the volume of the substrate.

Reduction of nitroaromatics (nitrobenzene and 2-methyl-1-nitronaphthalene) proceeded without induction period and with high yield, the turnover frequencies being in the range 489, 385 min^{-1} (Figure 5). It is remarkable that in our catalytic system the reduction of bulky molecules, such as 2-methyl-1-nitronaphthalene, is accomplished in 100% yield within 6 h under mild conditions. Kinetics results are shown in Figure 5. Given that oxidative addition is energetically unfeasible, heterolytic hydrogen cleavage must be involved in the catalytic hydrogenation reaction. The catalyst was reused without any reactivation at least four times. X-ray powder diffraction for the recovered material shows no change in the structure of the catalyst. After each cycle, the liquid phase separated from the reaction mixture was tested under the same reaction conditions for catalytic activity. The result showed a total inactivity of the liquid phase for the hydrogenation, and neither presence of In metal nor residues of BDC anion were detected in them.

Indium metal is recently being used as a reducing agent of nitroaromatic compounds but never in catalytic proportions.[22,23] It is worth pointing out that this new In(III) polymeric compound is effective at such a low metal/substrate ratio as 0.1%, which made this material a good alternative as heterogeneous catalyst for this reaction.

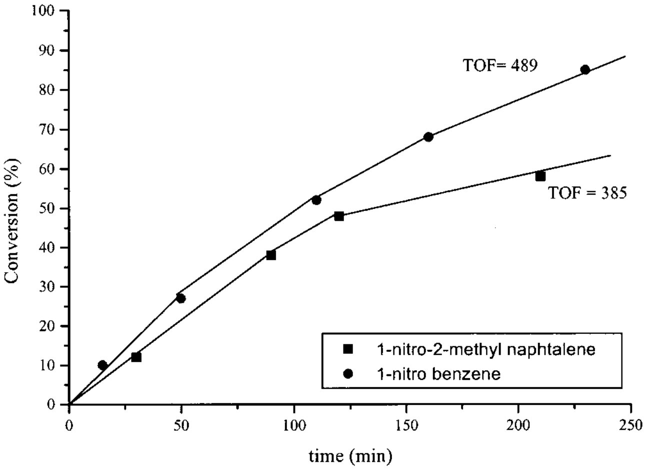

Figure 5. Kinetic profile for the reduction of nitroaromatics catalyzed by $In_2(OH)_3(BDC)_{1.5}$.

Table 3. Oxidation of Alkylphenylsulfides Catalyzed by $In_2(OH)_3(BDC)_{1.5}$ (5% Catalyst, Room Temperature)

substrate	convervsion % (h)	selectivity SO(%)	TOF[a]
methyphenylsulfide	100 (3)	73	273
(2-ethylbutyl)phenylsulfide	100 (6)	95	253

[a] Turnover frequency units: mmol substrate/mmol catalyst min.

Oxidation of Sulfides. The performance of the material as oxidation catalyst was tested with organic substrates such as methylphenylsulfide and (2-ethylbutyl)phenylsulfide. The activity and selectivity attained are collected in Table 3. The oxidations were carried out in the presence of catalytic amounts of the catalyst (5%) by using hydrogen peroxide (H_2O_2) as sacrificial oxidant in acetonitrile. This oxidant was examined because of its environmental acceptability, which depends mainly on the nature of its byproduct, water. The sulfide oxidations were performed at room temperature, because under these conditions it showed a high chemoselectivity, and sulfoxides were obtained as the main product of the reaction. Higher reaction temperatures lead to a dramatic decrease in the selectivity to sulfoxide. As can be concluded from the results, the substrates [methylphenylsulfide and (2-ethylbutyl)phenylsulfide] have shown a quite similar behavior in their oxidative transformations, suggesting that despite the differences in their structures they have the same reactivity. The selectivity data show that the sulfoxide is a primary and unstable product, while the corresponding sulfone appears as a secondary and stable product. The reactions showed a higher selectivity to sulfoxide for the largest studied substrate, (2-ethylbutyl)phenylsulfide. A series of blank experiments revealed that each component is essential for an effective catalytic reaction and the system is relatively unaffected by changing the order of mixing. Moreover, this catalyst can be recycled in successive runs by a simple filtration, without a significant loss of activity and selectivity. Chemical analysis performed after the reaction on the liquid phase showed no presence of In ions. This fact rules out the existence of In leaching and evidences the wholly heterogeneous character of the catalysis in the reaction. On the other hand, the catalyst with an excess of oxidant and/or long times of reaction yields, as the sole product, the corresponding sulfone with excellent yield.

In conclusion, in view of the showed results and given that the oxidation state of the indium cannot increase, a mechanism involving coordinative unsaturation, with either ligand dissociation or an increase in the coordination number of the indium, has to be responsible for the catalysis.

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Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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