CRYSTAL GROWTH & DESIGN
Communication
Cite This: *Cryst. Growth Des.* 2019, 19, 6053−6057
pubs.acs.org/crystal

Halide Directed Synthesis of an In-Derived Metal−Organic Framework with Two Unique Metal Centers and Isolation of Its Potential Synthetic Precursor

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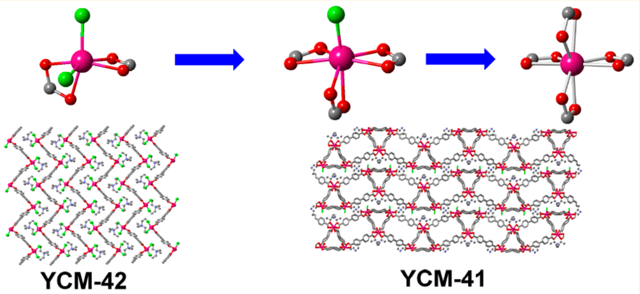
Supporting Information

ABSTRACT: The mechanism of formation of metal−organic frameworks (MOFs) is an emerging field, where each new discovery propels the field forward. Often, studies focus on studying nucleation events with advanced spectroscopy and microscopy techniques. Efforts to synthetically understand the molecular intermediates involved and their role in self-assembly are less common. Herein we report the synthesis of a MOF, **YCM-41** (YCM = Youngstown Crystalline Material), that contains two different In-nodes: one the standard $[In(CO_2R)_4]^-$ and the second of $[In(CO_2R)_3Cl]^-$. We hypothesize that the $[In(CO_2R)_3Cl]^-$ is a mechanistic intermediate in the synthesis of $[In(CO_2R)_4]^-$. Additionally, we report the isolation of 1-D coordination polymer, **YCM-42**, containing the previously unreported $[In(CO_2R)_2Cl_2]^-$ building unit. The 1-D herringbone structure of YCM-42 can be found in YCM-41. Finally, attempts to synthesize an isoreticular version of these structures led to the synthesis of the 1-D coordination polymer **YCM-51**, which contains a $[In(CO_2R)_2Cl_2F]^{2-}$ center.



Metal−organic frameworks (MOFs) are comprised of both inorganic and organic building units.[1] Frequently, the inorganic building unit is formed *in situ* from simple metal halide or metal nitrate precursors.[2] While the synthesis of the inorganic building unit is often controllable,[3−6] the mechanisms of formation of these building units and the framework as a whole are still not widely understood. Spectroscopic and computational approaches in mechanistic MOF chemistry primarily focus on crystal nucleation and growth.[7] Nakamura has observed prenucleation clusters of MOF-5 and MOF-2 using single-molecule atomic-resolution electron microscopy.[8] O'Hare demonstrated the intermediacy of different topologies in the synthesis of paddle-wheel MOFs using *in situ* powder X-ray diffraction (PXRD).[9] Weeks utilized UV resonance Raman to demonstrate the solution-phase formation of Co^{2+}−bipyridine interactions, implying that MOF-layer pillaring does not have to occur in the solid-state.[10] Glezakou has reported that carboxylates join the metals together first, before the bridging oxygen atoms are incorporated during formation of the Cr_3O cluster *in silico*.[11] Recent follow-up work revealed that there are over 300 chemical entities implicated in early-stage nucleation of MOFs containing the Cr_3O cluster.[12] Through molecular dynamics calculations, Kusalik showed that the complete formation of the Zn-paddlewheel is not necessary for the self-assembly of MOF-2.[13]

While spectroscopic and computational studies are critical to understanding MOF-formation mechanism, the synthesis and isolation of MOF-intermediates is a necessary complement to these studies. However, examples of MOFs containing "intermediate" inorganic building units, inorganic nodes that are partially formed and contain remnants of their metal halide/nitrate providence, are few. The formation of MOFs is often enthalpically driven, and thus the fully formed structure rests in an enthalpic minimum on the reaction coordinate.[14] This renders the isolation of MOF-intermediates and coordination polymers synthesized from these intermediates thermodynamically challenging.[15,16] We hypothesized that In-derived frameworks and their respective secondary building units (SBUs), when synthesized from In(III)-halides, would be an appropriate system to study due to the putative intermediacy and high bond dissociation energy of In-halide bonds[17] in the formation of $[In(CO_2R)_4]^-$ inorganic nodes (Figure 1).[18−22]

Previously, we reported the synthesis of In-derived coordination polymers YCM-22,[23] YCM-31, and YCM-32[24] (YCM = Youngstown Crystalline Material) containing $In(O_2CR)_2Cl_3$ and $In(O_2CR)_3Cl$ nodes, respectively. The

Received: October 1, 2019
Revised: October 8, 2019
Published: October 16, 2019

DOI: 10.1021/acs.cgd.9b01301
Cryst. Growth Des. 2019, 19, 6053−6057

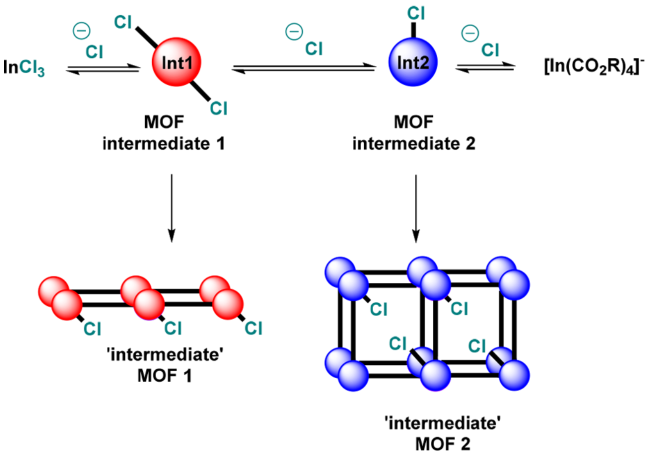


Figure 1. Proposed synthesis of In-derived "Intermediate MOFs".

halogenated In-metal centers of these frameworks and the previously reported $[\mathrm{In}(\kappa^2\text{-}\mathrm{O_2CAr})_2(\kappa^1\text{-}\mathrm{O_2CAr})\mathrm{Cl}(\mathrm{OH_2})]$,[25] $\mathrm{In}(\mu\text{-}\mathrm{O_2CAr}\text{-}\kappa\mathrm{O}{:}\kappa\mathrm{O'})_4(\mathrm{OH_2})\mathrm{Cl}$,[26] and $[\mathrm{InX_2(CO_2R)_2(pyr)}]^-$ (X = halide)[27] nodes inspired us to pursue the synthesis of additional halogenated In-derived frameworks and to examine their potential role in MOF formation. Herein we report the synthesis of an In-derived framework containing both $\mathrm{In(O_2CR)_3X}$ and the $\mathrm{In(O_2CR)_4}$ nodes, **YCM-41**. Additionally, two 1-dimensional coordination polymers were isolated, one containing the $\mathrm{In(O_2CR)_2Cl_2}$, **YCM-42**, which we hypothesize is a direct mechanistic precursor to YCM-41, and another containing a mixed halogenated center $\mathrm{In(O_2CR)_2Cl_2F}$ **YCM-51**.

When $\mathrm{InCl_3}$ is treated with 4,4′-biphenyldicarboxylic acid ($\mathrm{H_2BPDC}$) and 2 equiv (relative to indium) of tetraethylammonium chloride ($\mathrm{Et_4NCl}$) in DMF at 120 °C for 6 days, the framework YCM-41(Cl) containing both $[\mathrm{In(O_2CR)_3Cl}]^-$ and $\mathrm{In(O_2CR)_4}$ nodes in a 3:2 ratio is obtained (Figure 2).[28] Note that the term YCM-41 is the descriptor for the anionic framework of the molecular formula $\mathrm{C_{72}H_{46}X_2In_3O_{20}}$ (X = halogen) and does not contain information about guest cations or solvent molecules. Since treatment of $\mathrm{InCl_3}$ with $\mathrm{Et_4NCl}$ leads to initial $[\mathrm{InCl_4}]^-$ formation, the providence of the Cl-ligand on the In-center in YCM-41 can be traced to both the starting $\mathrm{InCl_3}$ and the $\mathrm{Et_4NCl}$ additive. YCM-41 is a periodic structure in which each repeating period is fourfold interpenetrated and are comprised of individual pseudo-2-dimensional *mcm* nets. The nets are composed of 24 Å × 15 Å pentagonal pores that are connected into "warped" hexagonal "half-bowl" geometries with a 97° pitch (based on In−In−In angles). Each In-center has four X-type ligands bound to the metal leading to a formal negative charge at indium. Every $[\mathrm{In(O_2CR)_3Cl}]^-$ node is bound to one additional $[\mathrm{In(O_2CR)_3Cl}]^-$ and two $[\mathrm{In(O_2CR)_4}]^-$ centers, while every $[\mathrm{In(O_2CR)_4}]^-$ is bound exclusively to $[\mathrm{In(O_2CR)_3Cl}]^-$ nodes. Since both $[\mathrm{In(O_2CR)_3Cl}]^-$ and $[\mathrm{In(O_2CR)_4}]^-$ are present in the MOF, we hypothesize that the $[\mathrm{In(O_2CR)_3Cl}]^-$ node may in fact be a chemical intermediate in the synthesis of the standard $[\mathrm{In(O_2CR)_4}]^-$ node. Supporting this, the previously reported MOF derived from BPDC and $[\mathrm{In(O_2CR)_4}]^-$ is also fourfold interpenetrated,[29] arguing that perhaps YCM-41 is a

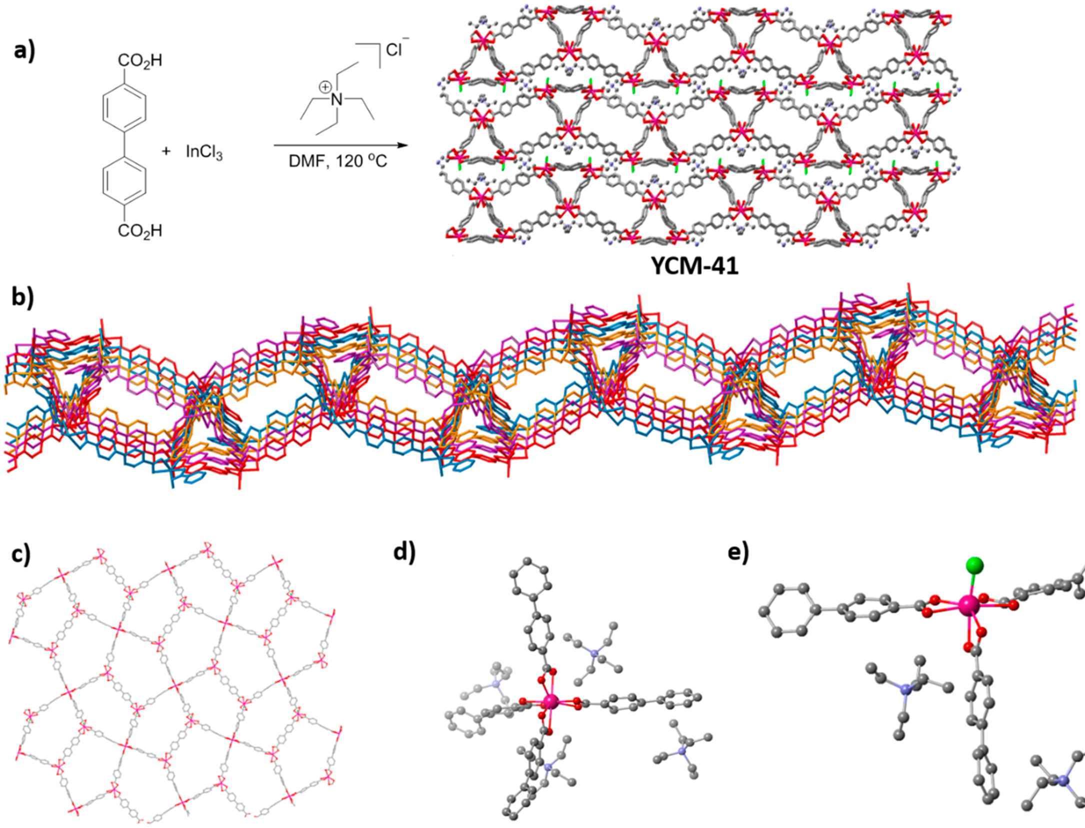


Figure 2. (a) Synthesis of YCM-41. (b) Color coded model of quadruple interpenetrated single period of YCM-41. (c) Single sheet of single period. (d) Depiction of $[\mathrm{In(CO_2R)_4}]^-$ node of YCM-41. (e) Depiction of $[\mathrm{In(CO_2R)_3Cl}]^-$ node of YCM-41.

self-assembly intermediate for that structure. During the preparation of this manuscript, Huang published the same architectural framework as YCM-41, albeit with $[Me_2NH_2]^+$ counterions in the pores, synthesized from $InCl_3$ and H_2BPDC in CH_3OH and DMF.[30]

Crystallographically, only two-thirds of the necessary charge balancing cations can be observed, all of which are $[Et_4N]^+$ cations participating in cation−π interactions with the arene of BPDC. NMR analysis of the digested MOF post synthesis revealed that $[Et_4N]^+$ is the only cation, and no $[Me_2NH_2]^+$, from DMF decomposition, is observed (Figure S2). YCM-41 can also be synthesized with Et_4NBr and $Et_4N(BF_4)$ as additives; however, single crystals of YCM-41 grown from Et_4NBr reveal an $[In(O_2CR)_3Br]^-$ node instead. The solvent stability of YCM-41 is consistent with other anionic In-derived MOFs, in that it is stable in polar organic solvents such as EtOH and CH_3CN for at least 8 days, but decomposes readily in 1 M HCl, 1 M NaOH, and water (Figure S3).

Strikingly, when $InCl_3$ is treated with 4,4′-biphenyldicarboxylic acid (H_2BPDC) and tetraethylammonium chloride (Et_4NCl) in a 3:2 DMF:dioxane solvent mixture at 120 °C for 3 days, a 1-D coordination polymer, YCM-42, is formed containing the $[In(CO_2R)_2Cl_2]^-$ node (Figure 3) in trace amounts. Note that the term YCM-42 is the descriptor for the anionic framework of the molecular formula $C_{14}H_8Cl_2InO_4$ and does not contain information about guest cations or solvent molecules. The 1-dimensional chains of YCM-42 assemble in the solid-state in a pseudoherringbone pattern with charge balancing $[Et_4N]^+$ ions occupying the interstitial space between the chains. Ma recently reported an In-derived MOF containing an $In(CO_2R)_2Cl_2$;[27] however, that particular node also contained an additional pyridyl ligand leading to a 5-coordinated indium center. To the best of our knowledge, YCM-42 contains the first four-coordinated In-center bound to two chlorides and two carboxylates. Unfortunately, efforts to consistently synthesize phase-pure YCM-42 have been in vain. We hypothesize that this can be attributed to $[In(O_2CR)_2Cl_2]^-$ being a putative intermediate in the synthesis of both $[In(O_2CR)_3Cl]^-$ and $[In(O_2CR)_4]^-$ akin to the transient intermediates that have been observed in the synthesis of MOF-5.[15] Additionally the 1-dimensional zigzag of YCM-42 can be found in the structure of YCM-41 (see Figure 4). This implies that while the node of YCM-42 is a chemical precursor to the nodes found in YCM-41, the supramolecular structure of YCM-42 is a potential supramolecular intermediate in the self-assembly of YCM-41. It is possible that the 1-D chains of YCM-42 initially form and are then cross-linked by BPDC and In to form YCM-41. Alternatively, the 1-D chains could be synthesized at the same time as the 2-dimensional sheets of YCM-42 are assembled. Which mechanistic path is optimal is unknown at this time.

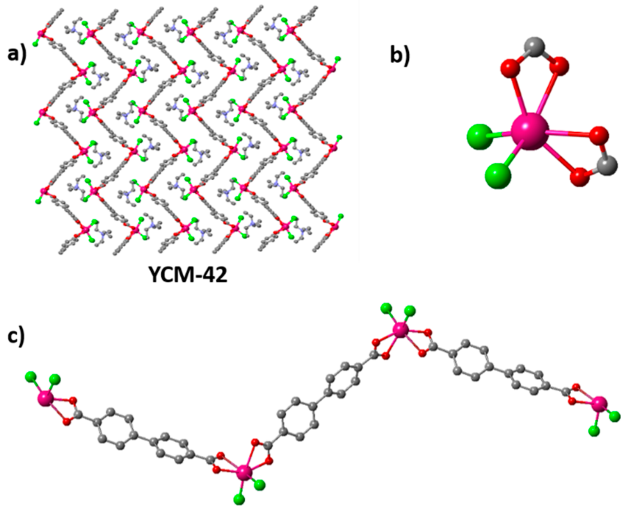


Figure 3. (a) Structure of YCM-42. (b) Depiction of $[In(CO_2R)_2Cl_2]$ node. (c) Depiction of single chain of YCM-42.

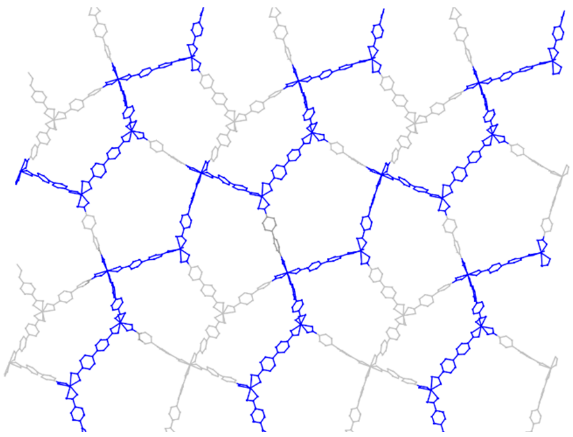


Figure 4. Depiction of single YCM-42 chains (blue) in structure of YCM-41.

Attempts to synthesize an isoreticular structure of YCM-41 were unsuccessful. Unfortunately, treatment of $InCl_3$ with terephthalic acid and Et_4NCl, Et_4NBr, and $Et_4N(BF_4)$ yielded the In-infinite chain derived structure, MIL-68(In). However, on certain occasions reactions using $Et_4N(BF_4)$ as an additive resulted in trace amounts of a 1-dimensional coordination polymer, YCM-51, containing a dianionic $[In(O_2CR)_2Cl_2F]^{2-}$ center (Figure 5). Note that the term YCM-51 is a descriptor for the dianionic coordination polymer of molecular formula $C_8H_4Cl_2FInO_4$ and does not contain information about guest cations or solvent. We hypothesize that the In−F bond is putatively established via fluoride transfer from the BF_4

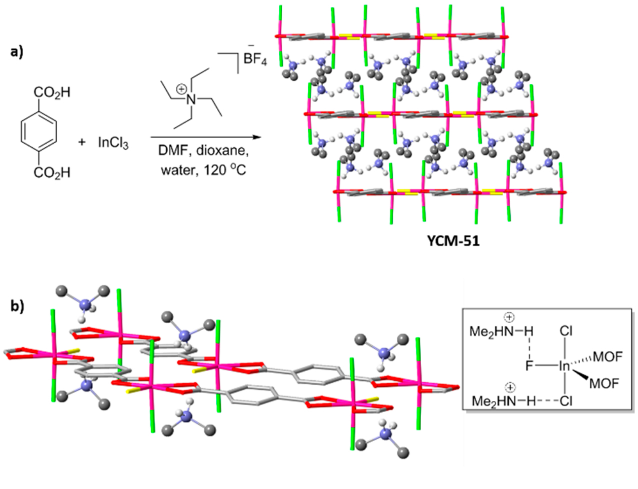


Figure 5. (a) Synthesis of YCM-51. (b) Two chains of YCM-51 (inset depicting hydrogen bonding of $Me_2NH_2^+$ with In-halide bonds.

counterion; however, deployment of Et_4NF as the additive only yields MIL-68. The penta-coordinate In-center in YCM-51 has pseudotrigonal bipyramidal geometry in which the Cl-atoms occupy the two axial positions and the F atom occupies the equatorial position. While YCM-51 is synthesized in the presence of $[Et_4N]^+$ cations, the only charge balancing cation observed in the structure is $[Me_2NH_2]^+$ which is putatively formed from DMF solvent decomposition. X-ray crystallography indicates that the cations are engaged in hydrogen bonding with the equatorial fluorides on indium. Unfortunately, our efforts to develop a phase-pure synthesis of YCM-51 have been unsuccessful. Using InF_3 or $InBr_3$ with Et_4NCl, Et_4NBr, or $Et_4N(BF_4)$ yielded either no reaction or MIL-68.

In summary, we report the synthesis of three In-derived materials: one periodic MOF (YCM-41) and two 1-dimensional coordination polymers (YCM-42 and YCM-51) containing halogenated anionic indium-centers. We hypothesize that these halogenated In-centers are in fact intermediates of the $[In(O_2CR)_4]^-$ node isolated in previously reported coordination polymers. The mechanistic implications of their isolation is being studied fully and the results of that work will be reported in due time.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.9b01301.

Experimental details, synthetic procedures, PXRD, and crystallographic information (PDF)

Accession Codes

CCDC 1954267−1954270 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was funded by NSF Grant DMRRUI: 1807462. The X-ray diffractometer was funded by NSF Grant DMR 1337296. We thank the team at ToposPro for their net analysis.

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DOI: 10.1021/acs.cgd.9b01301
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