

Mimicking Zeolite to Its Core: Porous Sodalite Cages as Hangers for Pendant Trimeric $M_3(OH)$ Clusters ($M = Mg, Mn, Co, Ni, Cd$)

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S Supporting Information

ABSTRACT: A new class of zeolite-type porous materials in which 3D frameworks are covalently functionalized with crystallographically ordered pendant metal clusters have been synthesized. This work demonstrates a new paradigm for and the feasibility of functionalizing zeolite-type frameworks through the conversion of extraframework sites in mineral zeolites into part of the framework for occupation by dangling metal clusters in metal–organic frameworks.

Crystalline porous materials comprise multiple families of crystalline solids rich in framework compositions, topologies, and functionalities.^{1–3} In particular, because of the industrial importance of zeolites, zeolite topologies have been the target of numerous synthetic efforts for over half a century.⁴ Despite the fact that a variety of chemical compositions have been explored, the general guiding principle, which is based on the mimicking of aluminosilicate structures through the assembly of 4-connected tetrahedral nodes (T-nodes) with 2-connected bridging ligands (e.g., O^{2-}), has remained unchanged.^{5–7} This strategy, while successful in creating many zeolite-type porous frameworks, has had limited success in creating functional metal sites on the framework. As a result, properties of zeolites (e.g., acidity, sorption) often rely on framework defects (e.g., Al–OH) or extraframework species (e.g., Li^+). A similar limitation in the case of functionalization of porous frameworks with inorganic clusters also exists in metal–organic frameworks (MOFs), in which covalent attachment of metal clusters to the framework is little known, even though the organic portion of MOFs can be postsynthetically modified and individual metal ions attached.⁸ There is thus a strong impetus to develop a new paradigm capable of functionalizing zeolite-like frameworks with various entities, including active metal clusters.

Other than the judicious choice of T-nodes, the strategy for the creation of zeolite-type nets relies critically on the notion of 2-connectedness of the cross-linking ligands (e.g., O^{2-}) between T-nodes, frequently with an added requirement of T–L–T angles (L = ligand) being close to 145° . The fact that extraframework cationic species (e.g., Na^+) in zeolites also bond with framework oxygen sites has been ignored entirely or in some cases rendered to the sole role of structure direction, such as charge balancing or pore filling. As shown here, the geometric pattern of extraframework cationic sites might reveal a possible path toward framework functionalization in MOFs.

In mineral sodalite, $[Na_4Cl][Al_3Si_3O_{12}]$ (Figure 1),⁹ for example, each sodalite cage contains four tetrahedrally arranged

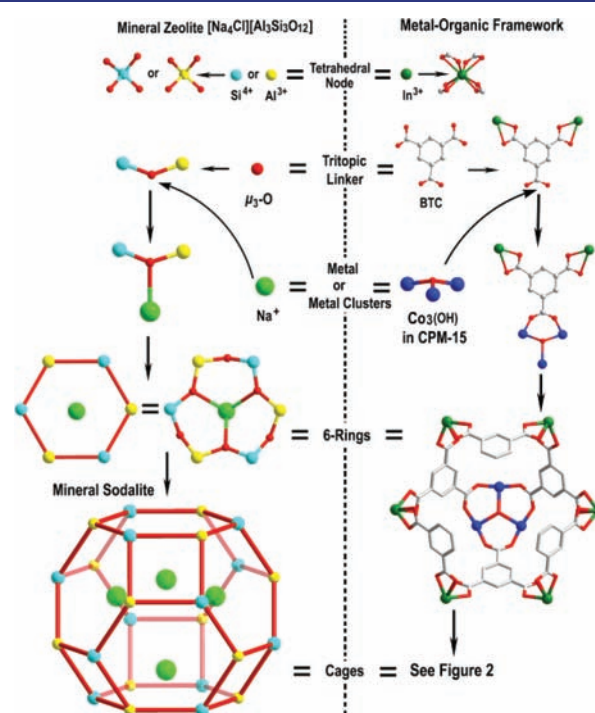


Figure 1. Illustration of the structural analogy between mineral sodalite and CPM-15 in the evolution from building blocks to cages, showing the structural equivalence between O^{2-} and BTC^{3-} and between Na^+ and $[Co_3(OH)]^{5+}$.

Na^+ sites. More pertinent to this work is the fact that these Na^+ sites are located adjacent to the six-membered rings (6-rings, i.e., six T-nodes in a ring) and that three nonadjacent oxygen sites (out of six) from such 6-rings bond to the same Na^+ site. We can describe this type of host–host (Al–O and Si–O) and host–guest (Na–O) bonding by treating these framework oxygen sites as being “tritopic”, each using two connections to form the zeolite framework and simultaneously using the third one to form an ionic bond with an extraframework Na^+ site in a concerted way that involves three oxygen sites from the same 6-ring.

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Here we report a series of porous materials that demonstrate the successful application of this new paradigm [Table S1 in the Supporting Information (SI)]: conversion of extraframework cationic sites in zeolites into functional pendant framework sites occupied by metal clusters. With our method, the simultaneous formation of zeolite frameworks and covalent attachment of transition- and non-transition-metal clusters is accomplished in a single step. Specifically, with this strategy, a low-cost trifunctional ligand [1,3,5-benzenetricarboxylate (BTC) in this work] is employed in combination with a mixed-metal ($\text{In}^{3+}/\text{M}^{2+}$) system. Since the members of this series are isostructural, only the structure of CPM-15-Co (CPM = crystalline porous material) is discussed here in detail.

As shown in Figure 1, the formation of the 4-connected zeolite framework is achieved by using two functional groups from the same BTC ligand to cross-link 4-connected T-nodes (monomeric In^{3+}), while the third functional group of BTC serves as an anchor point for a metal cluster. In this way, almost inconceivably, BTC and $\text{M}_3(\text{OH})$ clusters are structurally equivalent to O^{2-} and Na^+ in mineral sodalite, respectively. Thus, our strategy for the construction of MOFs effectively converts and integrates extraframework sodium sites into the covalent porous framework, making functionalization of the framework by metal clusters a synthetic endeavor that can perhaps be pre-designed by studying the cation distribution in various inorganic zeolites. The unusual chemistry of BTC has also been demonstrated in the $\text{Cu-BTC-CH}_3\text{OH-H}_2\text{O}$ system developed by Morris and co-workers,¹⁰ leading to a highly unusual chemical process: site-selective esterification of H_3BTC .

The crystal structure of CPM-15-Co determined from single-crystal X-ray analysis reveals it to have the formula $[(\text{CH}_3)_2\text{NH}_2]_4[\text{In}_6(\text{BTC})_{12}]_2[(\text{Co}_3\text{OH})_4(\text{H}_2\text{O})_{36}][(\text{In}_2\text{CoO})_4(\text{BTC})_4(\text{H}_2\text{O})_{12}] \cdot (\text{solvent})_x$ (based on two sodalite cages), where the parts expressed by the four sets of square brackets represent (a) counteranions, (b) sodalite cages, (c) the content of 50% of the sodalite cages, and (d) the content of the other 50% of the sodalite cages, respectively. The two types of sodalite cages present in equal numbers are denoted as SOD-A and SOD-B (Figure 2). Each SOD-A cage contains four pendant $[\text{Co}_3(\text{OH})]^{5+}$ trimers tetrahedrally arranged within the cage (same as the distribution of Na^+ sites in sodalite). Each trimer hangs from one 6-ring of SOD-A through three nonadjacent carboxyl groups and is thus 3-connected (a sodalite cage has six 4-rings and eight 6-rings, and most relevant to this work is the fact that the eight 6-rings can be considered as two sets of tetrahedrally distributed 6-rings). The exposed side of each trimer facing the cage center is occupied by as many as nine H_2O molecules (three per Co), which are potential active metal sites upon activation. It is worth noting that metal trimers in MOFs usually have connectivities ranging from 6 to 9, in comparison with the 3-connectedness in CPM-15.

In contrast to SOD-A, each SOD-B cage contains mixed In/Co metal trimers $[\text{In}_2\text{CoO}]^{6+}$, and their pattern of connectivity to the framework is similar to that of $[\text{Co}_3(\text{OH})]^{5+}$, except that the trimers in SOD-B are further linked by four intracage BTC ligands, similar to the Cr_3O - and In_3O -based supertetrahedra in MIL-100 and CPM-5, respectively.¹¹ The absence of intracage BTC ligands to link four $[\text{Co}_3(\text{OH})]^{5+}$ trimers in SOD-A is likely due to the smaller positive charge of $[\text{Co}_3(\text{OH})]^{5+}$ in comparison with $[\text{In}_2\text{CoO}]^{6+}$ trimers.

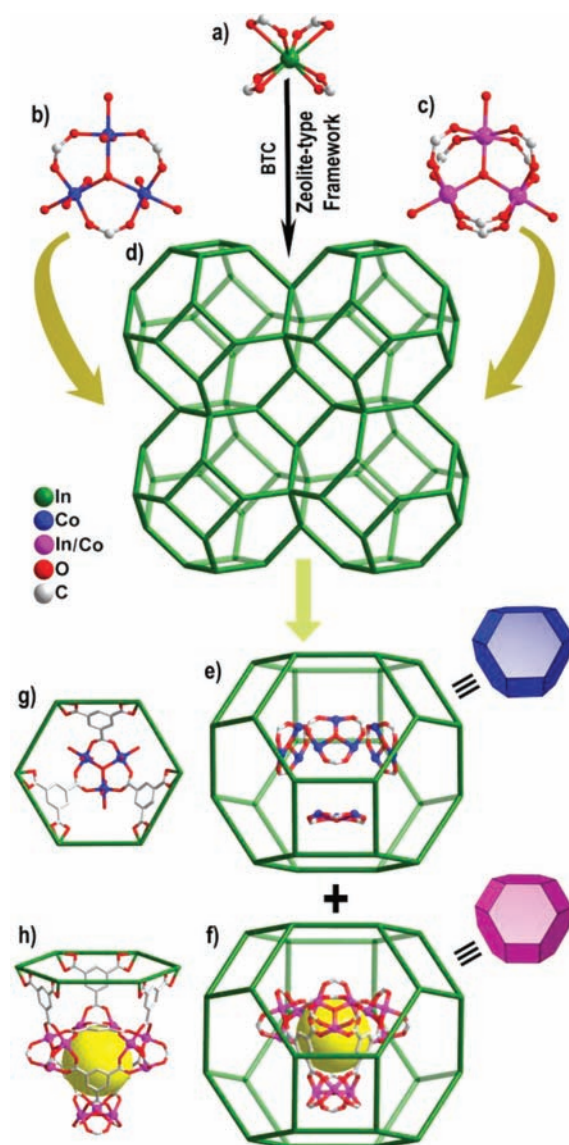


Figure 2. (a) $\text{In}(\text{CO}_2)_4$ monomer. (b) $\text{Co}_3(\text{OH})$ trimer. (c) In_2CoO trimer. (d) 3D sodalite framework. (e) SOD-A cage. (f) SOD-B cage. (g) Top and (h) side views (relative to the 6-ring) of metal clusters attached to the 6-rings of the sodalite cage, respectively.

One of the most interesting features of this work is the nonsymmetric bonding exhibited by the symmetrical BTC ligand (NSB-SL), which leads to the emulation of the mineral sodalite structure beyond just its 4-connected framework. We anticipate that this type of NSB-NL, as a general synthetic strategy, holds great promise for the development of new types of porous materials with previously unseen features and functions. It is thus important to analyze and understand the synthetic factors that lead to NSB-SL in this work. It is worth noting that BTC does also exhibit a strong tendency for symmetrical bonding, as demonstrated by the synthesis of a family of (3,4)-connected porous $[\text{In}_3(\text{BTC})_4]^{3-}$ C_3N_4 -type framework materials (denoted here as the CPM-1 series).¹² The symmetric bonding by BTC in CPM-1 is apparently due to the predominant role of the $[\text{In}(\text{RCOO})_4]^-$ monomer, which disfavors NSB-NL. In this work, however, NSB-NL occurs, perhaps because of our use of the mixed-metal system, which creates a nonsymmetric solution environment around the

symmetric BTC ligand through the coexistence of different possible units (e.g., $[\text{In}(\text{RCOO})_4]^-$ monomers and metal trimers such as $[\text{In}_3\text{O}]^{7+}$, $[\text{In}_2\text{CoO}]^{6+}$, and $[\text{Co}_3(\text{OH})]^{5+}$) with differing bonding requirements and charge-balancing properties. Among these units, the unique 4-connectedness of the $[\text{In}(\text{RCOO})_4]^-$ monomer leads to the formation of the In–BTC sodalite cage. On the other hand, while different trimers exhibit the same bonding geometry, they have different charges and compete for the attachment to the 6-rings of the sodalite cages, sometimes through the mediation of additional BTC ligands, as evidenced by the formation of both the SOD-A and SOD-B cages.

In a sodalite structure, each cage is surrounded by 14 other cages by sharing of either a 4-ring or a 6-ring. In a typical sodalite, the vertex of the guest tetrahedron (e.g., Na_4) points to the face center of another guest tetrahedron in the adjacent cage across from the 6-ring (the vertex-to-face or V–F pattern). However, CPM-15-Co is unlike anything known to date, and the unique distribution and orientation of the metal clusters lead to two additional types of polyhedral cages (Figure S1 in the SI) that further partition the pore space. In CPM-15-Co, each SOD-A cage shares its six 4-rings with six SOD-B cages and vice versa. However, across the eight 6-rings of each SOD-A cage are four SOD-A and four SOD-B cages (Figure 3a). An

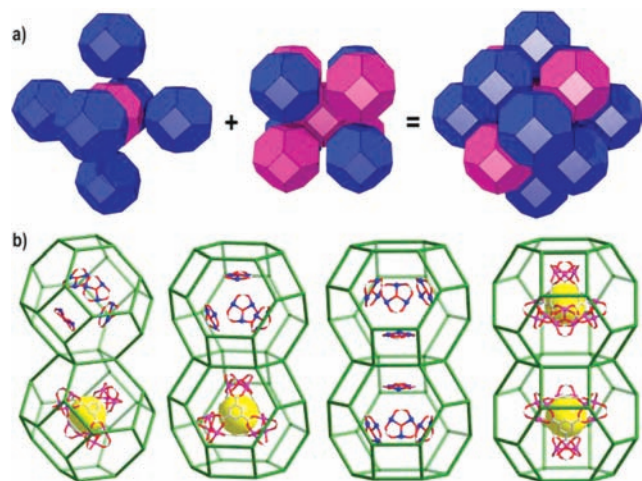


Figure 3. (a) 3D packing diagram of the two kinds of sodalite cages in CPM-15. (b) Four different types of intercage stacking resulting from the two different types of sodalite cages.

analysis of fourteen intercage patterns showed that there are four different arrangements involving two adjacent sodalite cages: SOD-A versus SOD-B (across a 4-ring), SOD-A versus SOD-B (across a 6-ring), SOD-A versus SOD-A (across a 6-ring), and SOD-B versus SOD-B (across a 6-ring) (Figure 3b). While the V–F pattern is found between SOD-A and SOD-B cages, the vertex-to-vertex pattern is present between two SOD-A cages, leading to a unique saucer-shaped cage centered at the middle of 6-rings (Figure S1a). In comparison, the face-to-face pattern exists between two SOD-B cages, creating a cuboctahedral cage (Figure S1c). These various types of intercage arrangements are likely dictated by one important observation: $[\text{Co}_3(\text{OH})]^{5+}$ trimers apparently prefer to be arranged on the two sides of the same 6-ring, and this tendency likely plays a critical role in the formation of CPM-15-Co.

CPM-15-Mg was selected for characterization of the porosity. Thermogravimetric analysis (TGA) of CPM-15-Mg showed

that the removal of solvent molecules occurred in the temperature range of 40–300 °C (Figure S6). Powder X-ray diffraction (PXRD) further confirmed that the crystal of CPM-15-Mg is stable and retains its crystallinity up to about 300 °C (Figure S7). CPM-15-Mg was degassed at 260 °C for 24 h under vacuum prior to the measurement. As shown in Figure 4,

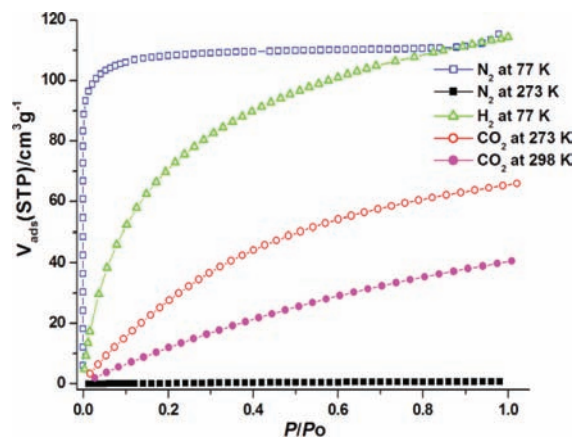


Figure 4. Gas adsorption isotherms of CPM-15-Mg.

N_2 sorption by CPM-15-Mg exhibited a type-I isotherm typical of materials having permanent microporosity. The Langmuir and Brunauer–Emmett–Teller surface areas were 474 and 398 m^2/g , respectively. A micropore volume of 0.169 cm^3/g (using Horvath–Kawazoe method) and a median pore size of 5.04 Å were calculated. CPM-15-Mg exhibited a significant uptake capacity for CO_2 . The CO_2 uptakes at 273 K and 1 atm and at 298 K and 1 atm reached 66.0 and 40.6 cm^3/g , respectively, which are comparable to that of the highly porous framework ZIF-69 (70 cm^3/g at 273 K and 1 atm).¹³ CPM-15-Mg can also adsorb a considerable amount of H_2 at 77 K and 1 atm (5.10 mmol/g, 1.02 wt %). Further N_2 sorption at 298 K by CPM-15-Mg indicated little uptake over the entire pressure range (0.75 cm^3/g at 1 atm). The CO_2/N_2 selectivity at 298 K was calculated to be 75:1 at 0.16 atm and 54:1 at 1 atm (or 118:1 at 0.16 atm and 85:1 at 1 atm calculated by weight). These values show that CPM-15-Mg exhibits a high selectivity for adsorption of CO_2 relative to N_2 .¹⁴

In conclusion, reported here are a series of highly unusual isostructural porous materials in which pendant trimeric metal clusters are covalently attached to the zeolite framework through 6-rings. To our knowledge, such crystallographically well-defined attachment of dangling metal clusters to the internal surface of zeolite frameworks has not been known before in any other types of porous materials. Through the use of metal–organic chemistry, our result demonstrates a potentially general and versatile method for the conversion of extraframework cationic sites in zeolites into covalently attached framework sites for occupation by metal clusters. This work shows that the structural analogy between mineral zeolites and MOFs goes beyond just the 4-connected framework. In this work, the 6-rings have been shown to play a key role in the attachment of metal clusters. Considering that 6-rings are a prominent feature in many zeolites, including the commercially important zeolites A and X/Y, it might be possible to extend this strategy to other zeolite structure types. The extension of this strategy to other ring sizes such as 4-, 8-, and 12-rings might allow other types of metal clusters to be

attached as well, which would greatly expand the versatility and utility of this synthetic method.

■ ASSOCIATED CONTENT

■ Supporting Information

Syntheses, TGA, IR, EDS, and XRD characterizations, CIF files, and additional structural figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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