

Porous Coordination Polymers

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Porous materials such as zeolites can reversibly absorb molecules and are widely used in many processes such as absorption of gas molecules, catalysis, and ion-exchange. Porous materials used in such processes are often size and shape selective, and in catalysis they are acid catalysts. Porous coordination polymers have unique characteristics because of the transition metals and organic ligands in their frameworks, and they can absorb molecules based on the functional groups of guests. While there are many examples of porous materials based on inorganic materials, functional frameworks consisting of both organic ligands and metal centers¹⁻⁶ are rare. The major challenges in producing these compounds are unstable frameworks in the absence of guest molecules, and interpenetrated networks that reduce the pore dimensions.⁷⁻¹⁰

In 1897, Hofmann and Küspert reported the first attempt to synthesize a porous coordination polymer, $\text{Ni}(\text{CN})_2\text{NH}_3 \cdot \text{C}_6\text{H}_6$, which is now known as Hofmann's benzene clathrate.^{11,12} In this compound, the benzene guest molecules are located between the two layers of square-planar nickel cyanide extended structure.^{13,14} The $\text{Ni}(\text{CN})_2\text{NH}_3$ host was later found to selectively incorporate aromatic compounds such as benzene, aniline, phenol, thiophene, pyrrole, and furan, but not alkyl-, dialkyl-, or halo-substituted benzenes, naphthalene, resorcinol, and toluidines.¹² Hence, the selectivity exhibited by the Hofmann-type clathrates is based on the size of the pores in the host and size of the guest molecules.

In more recent examples of porous coordination polymers, the selectivity toward the guest molecules does not only depend on the size and the shape of the reactants, but also on the chemical interactions between the host and the guest. For example, a three-dimensional porous solid $\text{Zn}_2(\text{BTC})(\text{NO}_3) \cdot (\text{H}_2\text{O})(\text{C}_2\text{H}_5\text{OH})_5$ (**1**) (BTC = 1,3,5-tribenzene-carboxylate)^{6,15,16} can selectively absorb alcohols. This extended solid has channels of 14 Å cross section, which account for nearly 44% of the structure. The nitrate anions are tightly bound and cannot be exchanged, but some of the ethanol and water molecules can be removed from the channels at room temperature to give $\text{Zn}_2(\text{BTC})(\text{NO}_3) \cdot (\text{H}_2\text{O})_{0.5}(\text{C}_2\text{H}_5\text{OH})$. Those guest molecules can be reversibly absorbed, and the framework is unchanged as confirmed by the presence of the same intense XRPD lines seen in the solvated solid **1**. It is proposed that **1** has high affinity for nonsterically hindered alcohols because these guest molecules can access and interact with the Zn(II) centers.

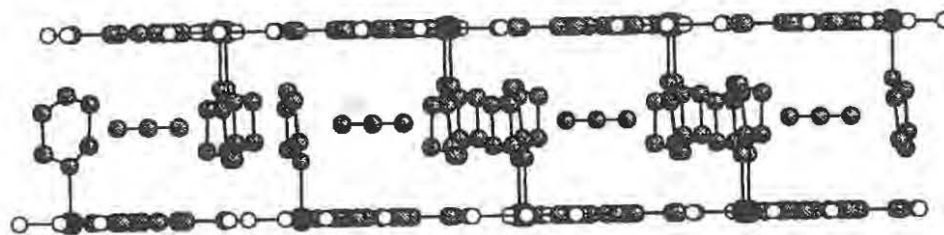


Figure 1

Both $\text{Co}(\text{HBTC})(\text{NC}_5\text{H}_5)_2 \cdot 2/3\text{NC}_5\text{H}_5$ (**2**)⁴ and 1,3,5-tris(4-ethynylbenzenenitrile)-benzene $\cdot\text{AgO}_3\text{SCF}_3$ (**3**)^{1,8} can selectively accommodate aromatic compounds. Compound **2** is composed of rigid layers of cobalt-carboxylate, forming $7 \times 10 \text{ \AA}$ rectangular channels where guest molecules reside (Figure 1). The guest pyridine molecules can be removed at $200 \text{ }^\circ\text{C}$ and the XRPD pattern of the resulting compound shows that the original framework is preserved. The resulting compound is subjected to absorption studies of various compounds and was shown to selectively bind aromatic compounds. Compound **3** has six interpenetrated ThSi_2 -type networks with hexagonal channels of $15 \times 22 \text{ \AA}$. This solid also retains its structure upon loss of the guest molecules, and the host can selectively incorporate aromatic molecules such as *m*-xylene over cyclooctane. The binding characteristics of **2** and **3** are the consequence of π -stacking of guest molecules in the cavities, since in both compounds the channels are primarily aromatic in nature.

Applications of porous coordination compounds in catalysis,^{17,18} separation of chiral compounds,¹⁹ sensors²⁰ still remain mostly uninvestigated at present.

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