

## Functional Organic Analogues of Zeolites Based on Metal–Organic Coordination Frameworks\*\*

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*Dedicated to Professor Roald Hoffmann on the occasion of his 60th birthday*

Supramolecular chemistry has reached a stage at which it is possible to select molecular building blocks that will assemble into structures with specific and desired network topologies, so that a rational design of molecular solids with potentially interesting properties is possible.<sup>[1]</sup> Recent efforts are being undertaken to generate three-dimensional (3-D) organic and metal–organic porous frameworks by the molecular building block approach. Of special interest is the search for stable microporous organic networks that exhibit reversible guest exchange and possibly selective catalytic activity. So far, no practical uses have emerged, but hopes are running high, and potential applications appear very promising. Construction of inner cavities and channels that are mainly surrounded by organic components is attractive, since the shape, size, and function of the cavity then become designable.<sup>[2]</sup> There is much interest in tailoring the geometry and the hydrophilic and hydrophobic character of the pores.<sup>[3]</sup> However, the key feature is not only the incorporation of guest molecules but also their reversible exchange. Here the present state of research concerning this crucial aspect is summarized.

Research on intercalation has concentrated largely on nanoporous inorganic materials such as aluminosilicates (zeolites), aluminophosphates, pillared clays, and graphite—all of which have been known for a long time.<sup>[4]</sup> Porous solids such as zeolites, which can now be “engineered” to some extent, are already important materials and find widespread application in adsorption (molecular sieves), shape- and size-selective heterogeneous catalysis, and ion exchange. An important aspect of zeolites is their structural stability, which allows guest concentrations to range from zero (empty host) to a maximum value (saturation).<sup>[5]</sup>

The goal in the search for organic porous frameworks is not simply to mimic inorganic materials such as zeolites by using different building blocks. Some of the properties of organic compounds, such as low thermal stability and low Lewis acidity,

are inherently different. Instead it is thought that organic networks should complement the inorganic ones since they exhibit properties that are not displayed by zeolites (for example chirality). The term “zeolite analogues” in connection with organic frameworks is not meant to imply that the full functionality of zeolites should be reproduced, rather it refers to the molecular-sieve character of zeolites, reversible guest removal, and the stability of the host framework in the absence of guest molecules.

Various research projects are currently concerned with the construction of channeled organic, metal–organic, and inorganic solids with a chemical architecture and, possibly, a catalytic activity that differ from those of zeolites. One approach involves porous metal organophosphates and organophosphonates in which the organic groups cover the internal surfaces.<sup>[3, 6, 7]</sup> Another variant combines the porous framework of zeolites with the catalytic activity of transition metal complexes by encapsulating molecular transition metal complexes in the pores of zeolites. Such an immobilization of metal complexes in a zeolite matrix should mimic the active center of enzymes.<sup>[8]</sup> A particularly intriguing strategy is to use covalent coordinative bonds and organic or inorganic ligands as links between metal ions. Different metal ions, various coordination geometries (such as octahedral, tetrahedral, or square planar), and numerous ligands provide a wide range of possibilities for connecting metal ions together to construct metal–organic frameworks. Covalent metal–organic lattices offer several possible advantages over their purely organic counterparts, including greater mechanical strength and the presence of catalytically active transition metals. An attractive feature of inorganic complexes is the availability of 90° joints for constructing a polymeric framework with macrocyclic boxes<sup>[9]</sup> as well as a potentially interesting interplay of hydrophobic and hydrophilic regions and interactions.<sup>[10]</sup> The synthesis or self-organization of these coordination polymers is achieved by combining the appropriate metal salt and a tailored ligand in a suitable solvent. The reaction proceeds under mild conditions, often spontaneously. The metal centers in a coordination polymer may be thought of as an assembling and templating species for the organic (ligand) groups.

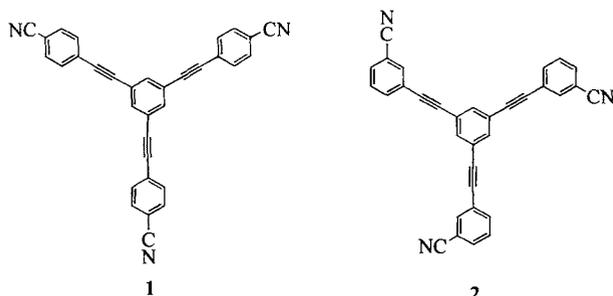
A large number of static metal–ligand frameworks and host–guest structures are known, but a reversible guest exchange or chemical transformations of the guest inside a coordination-

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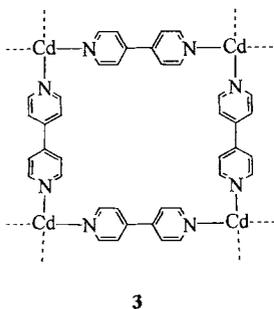
polymer framework has been described for only a few. Layered materials with channels perpendicular to the layers, such as in the first five examples, appear to be most promising as functional organic analogues of zeolites. The structural descriptions seldom include a detailed picture of the host-guest interactions, in part due to disorder. Only the building blocks will be illustrated here; for the often complicated 3-D networks see the original literature. The solid-state structure of  $[\text{Ag}(\text{TEB})\text{CF}_3\text{SO}_3] \cdot 2\text{C}_6\text{H}_6$  [(TEB = 1,3,5-tris(4-ethynylbenzotrile)benzene, **1**) exhibits hexagonal 15 Å channels,<sup>[11]</sup> which are created in spite of the interpenetration of six independent 3-D networks. The crystals are porous to benzene exchange; storage in  $\text{C}_6\text{D}_6$  led to the formation of the deuteriosolvate, as monitored by NMR spectroscopy. Dissolution and reformation of the lattice does not occur, as shown by X-ray powder diffractometry (XRPD).<sup>[12]</sup>

The silver triflate complex with the related tridentate ligand 1,3,5-tris(3-ethynylbenzotrile)benzene (**2**) forms a 2-D coordi-



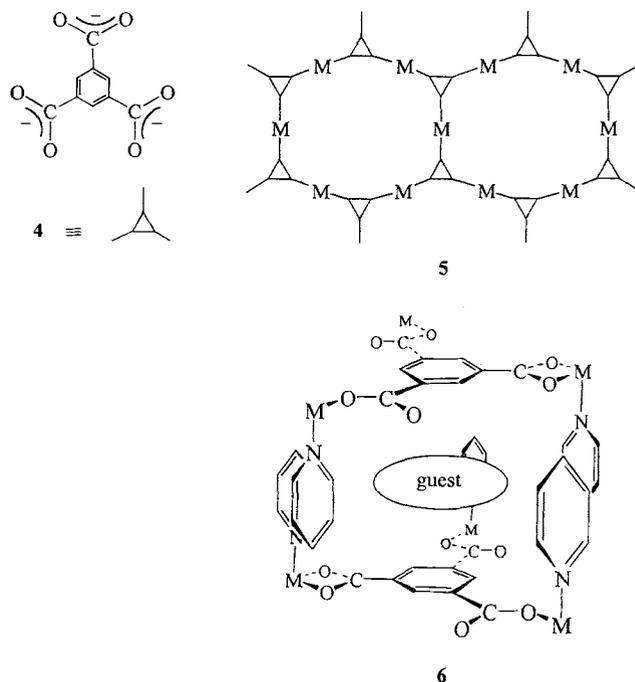
nation network that incorporates benzene molecules in channels running oblique to the layer plane. Of the 16 benzene molecules in the unit cell, four are lost reversibly at 110 °C (thermogravimetric analysis) without loss of crystallinity or a phase transition of the host structure, as shown by the optical transparency and XRPD. The remaining 12 benzene molecules are lost in a solid-to-solid phase transition at 145 °C, but even here subsequent cooling of the sample under a benzene atmosphere leads to the reabsorption of benzene and restoration of the original solid phase.<sup>[13]</sup>

The organic linkages can also be of smaller size, for example 4,4'-bipyridine groups. The 2-D square-network material  $\frac{2}{3}\{[\text{Cd}(4,4'\text{-bipyridine})_2](\text{NO}_3)_2\}$  (**3**), which contains microchannels perpendicular to the layers ( $\text{Cd} \cdots \text{Cd}$  11.8 Å), readily incorporates aromatic guests with high shape selectivity and catalyzes cyanosilylation of aldehydes.<sup>[2]</sup>



**4**).<sup>[14]</sup> Inclusion of ammonia into the solid was also demonstrated, whereas larger molecules and those without a reactive electron lone pair were prevented from entering the channels. The

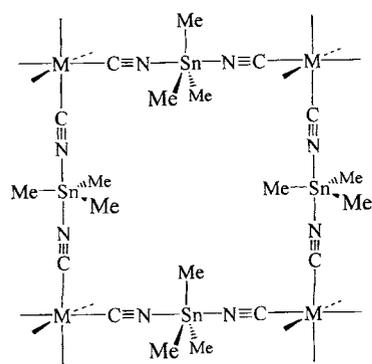
2-D metal-ligand assembly **5** with 1-D channels was proposed for the porous solid.<sup>[15]</sup> The same metal-BTC building block, but with two additional pyridine ligands at the metal center, gives the layer structure **6** in which the pyridine ligands act as



spacers between the layers. In the resulting  $7 \times 10 \text{ \AA}^{[11]}$  rectangular channels, aromatic guests are accommodated and can be reversibly removed. According to optical microscopy, the single crystals retain their morphology and crystallinity upon loss of the guests. IR spectroscopy showed that aromatic molecule such as benzene, nitrobenzene, cyanobenzene, and chlorobenzene are selectively absorbed from mixtures with nonaromatic compounds. The crystal lattice is thermally stable up to 350 °C.<sup>[15]</sup>

An earlier study already showed that formation of a fully covalently interconnected 2-D or 3-D metal-organic network or coordination polymer is not a prerequisite for porosity and reversible guest exchange. The layered  $\beta$ -structure composed of discrete octahedral  $[\text{Ni}(\text{NCS})_2(4\text{-methylpyridine})_4]$  complexes forms inclusion compounds with aromatic guests and retains its porosity in the absence of the guest molecules. Thermodynamic and kinetic data for the uptake of different guests were collected, and sorption equilibria in systems containing two competing guests studied.<sup>[16]</sup> Furthermore, this and the next example illustrate that zeolite-type behavior of metal-organic host lattices was occasionally observed prior to the recent surge in interest: A partly reversible intercalation of ferrocene in the 3-D network of  $\frac{3}{2}[\text{Fe}^{\text{III}}(\mu\text{-CN-SnMe}_3\text{-NC})_3]$  was described almost ten years ago. It was also demonstrated by XRPD that ferrocene can diffuse through the  $6.8 \times 6.8 \text{ \AA}^{[11]}$  channels of the analogous network of  $\frac{3}{2}[\text{Co}^{\text{III}}(\mu\text{-CN-SnMe}_3\text{-NC})_3](7)$ .<sup>[17]</sup>

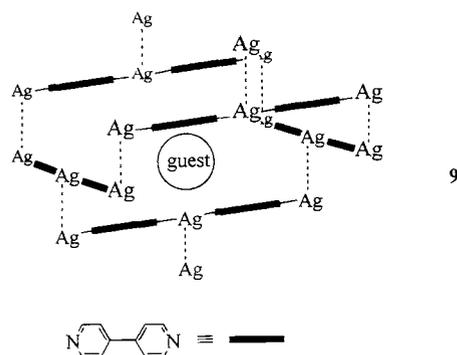
Not only neutral guest molecules but also lattice counterions can be removed: Crystals of  $[\text{Cu}(\mathbf{8})\text{BF}_4 \cdot x\text{C}_6\text{H}_5\text{NO}_2]$  were shown by IR spectroscopy to undergo anion exchange with  $\text{PF}_6^-$ . The metal-ligand moiety forms a diamond-related framework with no interpenetration and very large adamantane-like



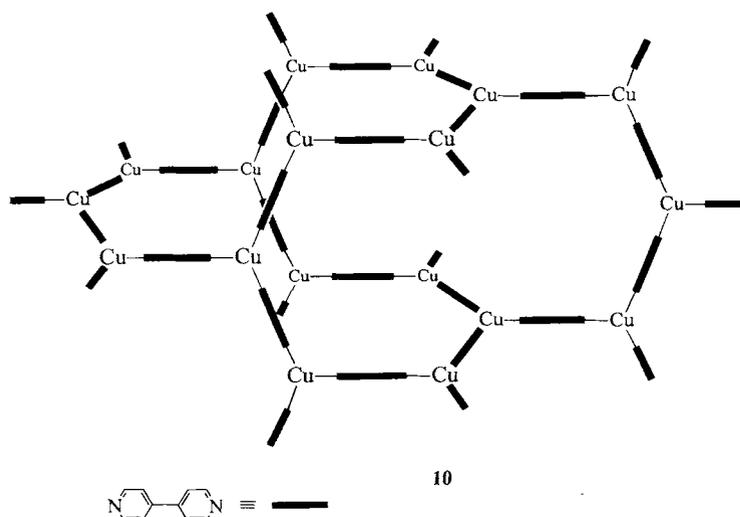
M = Fe, Co

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cavities<sup>[18]</sup> of about 1500 Å<sup>3</sup> (estimated from the space diagonals). The structure of [Ag(4,4'-bipyridine)NO<sub>3</sub>] contains extended linear silver–ligand chains, which are cross-linked by Ag...Ag contacts (9) to give extended 23 × 6 Å<sup>[11]</sup> channels, in



spite of the interpenetration of three different frameworks.<sup>[19]</sup> These channels are occupied by the nitrate “guests”, which can undergo reversible exchange with PF<sub>6</sub><sup>-</sup>, MoO<sub>4</sub><sup>2-</sup>, BF<sub>4</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> (monitored by IR spectroscopy and XRPD). The 4,4'-bipyridine ligand also connects Cu<sup>I</sup> centers in a trigonal-planar geometry and thereby allows formation of the open framework 10 in [Cu(4,4'-bipyridine)<sub>1.5</sub>NO<sub>3</sub>(H<sub>2</sub>O)<sub>1.25</sub>]. Since six of these



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frameworks interpenetrate each other but do not fill all the available voids, that rectangular channels (8 × 6 and 4 × 5 Å<sup>[11]</sup>) remain. These channels are occupied by the nitrate anions, which according to IR spectroscopy and elemental analysis undergo exchange with SO<sub>4</sub><sup>2-</sup> and BF<sub>4</sub><sup>-</sup>.<sup>[20]</sup>

In the layered porous structure of Na<sub>2</sub>[PhMe<sub>3</sub>N][Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sub>2</sub>Cl · 5 H<sub>2</sub>O, partial removal of the cationic templates (PhMe<sub>3</sub>N<sup>+</sup>) by cation exchange at room temperature and complete removal by thermal methods are apparently possible without loss of crystallinity. The [Na<sub>2</sub>Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>-</sup> moiety forms cylindrical pores of approximately 7 Å diameter and 3 Å<sup>[11]</sup> depth.<sup>[21]</sup>

From the examples given it becomes clear that nitrogen- and CN-containing ligands (nitriles) feature prominently as the organic building blocks. Building blocks for coordination networks are most often rigid bridging ligands, either linear or disk-shaped trigonal-planar; flexible ligands are used less often. Porphyrins and phthalocyanines have also been suggested as building blocks for microporous networks because of their relative rigidity and large size as well as their ready incorporation of a wide range of metal centers.<sup>[22]</sup>

Organic zeolite analogues promise a new range of applications, for example in pharmaceutical manufacture, molecular sieves, and sensors. A fascinating aspect is the potential to control the host–guest chemistry of the framework by tailoring the building blocks by including binding properties of functional organic groups that are not available in inorganic zeolites. One could imagine incorporating enantiomerically pure chiral groups to obtain microporous materials for enantiomer separation, chiral synthesis, and product-specific catalysis.<sup>[21, 23]</sup> However, before these ambitious goals can be achieved certain hurdles must be overcome. The basic problems of inclusion crystals based on an organic host lattice are that they tend to lose their crystallinity and undergo collapse of the void spaces on removal of the (reinforcing) guest molecules from the pores.<sup>[22]</sup> Furthermore, the guest may be entrapped in a clathrasil-like fashion inside the framework of the host without the possibility of diffusing through the lattice.<sup>[11]</sup> Nature tends to avoid vacuum, and identical copies interpenetrate to fill space are obtained rather than a single network.<sup>[24]</sup> Interpenetration, which arises from the necessity to fill the empty spaces inside the large cages, is the rule rather than the exception in these species. Seldom do the interpenetrating networks create large cavities.<sup>[25]</sup>

The design and synthesis of new polymeric framework materials containing cavities capable of taking up molecular substructures in a shape- and/or size-selective manner is a continuing challenge. Selective incorporation of metal ions as integral components of such frameworks offers additional factors (electron transfer) that can be exploited in stimulating substrate reactivity. The area of coordination polymers, which can also be seen as a meeting ground for the subdisciplines of molecular and solid-state inorganic chemistry, brings together synthetic techniques and analytical methods for designing and investigating extended structures with specific physical properties by low-temperature reactions.<sup>[7]</sup>

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## Harmony and Dissonance in the Concert of Proton Motions

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The motion of a proton between donor and acceptor atoms is one of the simplest chemical reactions, and an overall reaction involving two such motions within the same molecular array represents the simplest case in which to consider the coupling of two chemical processes; do they occur simultaneously in time (concertedly) or serially in time (in a stepwise manner)?<sup>[1]</sup> Reactions in which multiple (often two) proton-transfer events among electronegative atoms such as O, N, and S accompany bonding changes in a framework of atoms heavier than H are of interest in biology as well as chemistry, for example in the action of enzymes<sup>[2]</sup> and in tautomerization reactions in nucleic-acid base pairs.<sup>[3]</sup> Several recent studies have begun to illuminate the manner in which the molecular choice between concerted and stepwise motion of the protons is made.

The history of this subject began some time ago. In 1952 Swain and Brown<sup>[4]</sup> showed that reagents with both proton-donor and proton-acceptor sites can accelerate with extraordinary power reactions that require both proton donation and proton removal. They denoted the phenomenon polyfunctional

catalysis, which is exemplified by the catalysis of an elementary ring-opening step in the mutarotation of glucose (or its 2,3,4,6-tetramethyl derivative) by 2-pyridone. The ring-opening reaction of glucose derivatives involves more than the motion of the two protons. The internal C—O  $\sigma$  bond of the pyranose ring is cleaved, and a  $\pi$  bond added to the external C—O  $\sigma$  bond. If the formation and fission of C—O bonds (heavy-atom reorganization) were coupled to the transfer of the protons between the glucose molecule and the catalyst (which need not be true),<sup>[2]</sup> such a reaction could proceed by any of three pathways from reactant state **1** to product state **3**, which can take place via the activated complex **2** and the intermediate compounds **4** and **5**.

In reactions through **4** and **5**, the motions of the two protons between their bonding partners occur in a stepwise manner via two transition states that come before and after the intermediates along the reaction pathway. In a reaction through **2** the motions are concerted, and there is no intermediate. Swain and Brown concluded from the extraordinary catalytic activity of bifunctional compounds that the concerted pathway was preferred. This follows from the fact that 2-pyridone would function only as a very weak general base in the reaction leading to **4** and only as a very weak general acid in the reaction leading to **5**. Only in transition state **2** for the concerted reaction is the cooperative acid–base enhancement characteristic of bifunctional catalysts capable of expression. Rony and co-workers<sup>[5]</sup>

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