METAL-ORGANIC FRAMEWORKS

Design and Application

Edited by

LEONARD R. MacGILLIVRAY
University of Iowa

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PREFACE

The field of metal-organic frameworks, or MOFs, is undergoing accelerated and sustained growth. I personally became acquainted with MOFs, or more generally coordination polymers, as an undergraduate research student while at Saint Mary's University, Halifax, Nova Scotia, Canada, from 1991 to 1994. The process of mixing readily available metal precursors with organic linkers—many of which fell under the heading of being commercially available—to produce a wide array of extended frameworks clearly then, and now, captured the imagination of chemists and materials scientists worldwide.

From a fundamental standpoint, there is an important link between MOF chemistry and the field of inorganic chemistry. In many ways, MOF chemistry enables chemists to connect previously existing coordination complexes so as to make a conceptual link into the field of materials chemistry. This link has now evolved to afford applications ranging from catalysis to energy storage. Organic chemists are also able to contribute to the mix by crafting ligands with properties that one ultimately plans to express within the walls of MOFs. Solid-state chemists and X-ray crystallographers provide insights into the structures of MOFs so that the process of designing and synthesizing MOFs can be refined so as to ultimately control a targeted property and give rise to function.

My personal draw to MOFs was, in retrospect, also inspired by the field of supramolecular chemistry, particularly as it relates to the rational design of solids, or crystal engineering. The early 1990s witnessed supramolecular chemistry envelop the process of self-assembly, with a crystal being regarded as a supermolecule par excellence.[1] Metal–ligand bonding is reversible and, thus, fits within the realm of supramolecular chemistry. Self-assembly involves subunits of a larger superstructure

being repeated in zero-dimensional (0D), 1D, 2D, or 3D space, with the solid state being a perfect resting place for intermolecular forces to dominate. Today, many of the boundaries between these areas have become increasingly more difficult to distinguish, which can be expected as more is being uncovered and as more emphasis is placed on properties and function.

It is, thus, with great pleasure that I am able to assemble a multi-author monograph that includes authoritative contributions from leading research laboratories in the field of MOF chemistry. My goal is to provide insights into where the field of MOFs began to take root and provide an account of the fundamentals that define where the field has come and is able to go. Indeed, MOFs provide chemists a means to think about how to utilize coordination space to mimic the chemistry of zeolites with an added degree of organic function. These possibilities have become apparent in key developments and important advances that are outlined in the chapters that follow.

Fujita (Chapter 1) and Eddaoudi (Chapter 2), for example, document the first reports of MOFs, or coordination networks, particularly those that exhibit catalysis, the emergence of heteroaromatic ligands, and how carboxylates provided an important entry to increasingly robust solids. Batten (Chapter 3) demonstrates a role of symmetry in defining and understanding the simple and complex frameworks that result from the solid-state assembly process that affords a MOF. Next, Schroder (Chapter 4) addresses the design and synthesis of extended frameworks of increasingly structural complexity in the form of highly connected MOFs based on lanthanide ions. Kitagawa (Chapter 5) then shows how the internal structures of coordination networks can be rationally modified and tailored with organic groups while Lin (Chapter 6) documents some of the first systematic applications of MOFs as they relate to the generation of nonlinear optic materials. A great challenge facing mankind is making efficient use of energy. MOFs have emerged as potentially useful platforms for facing this challenge in the form of gas storage, separation, and conversion. Thus, Kim (Chapter 7) and Zhou (Chapter 8) address how MOFs interact with small gas molecules (e.g., H_2) and how these materials may be integrated into schemes for energy utilization. In a related topic, Friscic (Chapter 9) tackles the emerging issue of mechanochemical, or solvent-free, "green" preparation of MOFs while work by our group demonstrates how the walls of extended frameworks can be designed to serve as platforms for light-induced chemical reactions (Chapter 10). Finally, Snurr (Chapter 11) addresses how the field of computational chemistry can be used to understand, and ultimately, aide the design of MOFs, with targeted applications in separations, gas uptake, and materials characterization. Carefully chosen references serve to guide the reader through the extensive literature, which makes the field accessible to a wide and varied audience.

My initial interests in the chemistry of MOFs, and supramolecular chemistry and solid-state chemistry in general, stemmed from an experience as an undergraduate researcher. It is for this reason that I dedicate this monograph to the

undergraduate research experience and to all of those that support undergraduate research.

LEONARD R. MACGILLIVRAY

Iowa City, IA
March 2010

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1 Dunitz, J. D. *Pure Appl. Chem.* **1991**, *63*, 177.

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FROM HOFMANN COMPLEXES TO ORGANIC COORDINATION NETWORKS

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1.1 INTRODUCTION

Recently, there has been a considerable upsurge in the study of porous hybrid organic–inorganic materials referred as *organic coordination networks*. Porous organic coordination networks can be prepared via self-assembly of a connector (a metal) and a link (a ligand) where connectors and ligands are bound together through a metal–ligand bond to form porous crystalline structures. It is in the pores that a wide range of processes can be carried out. One salient feature of coordination networks is the possibility to *design* the pores. Now it is possible to create pores with determined sizes just by selecting ligands with determined shapes, and particular environments through functionalization of the ligands. Therefore, certain reactions that are not possible to be carried out in solution are now being carried out within the porous space.

Another feature of organic coordination networks is their flexibility, which differentiates them from the robust frameworks of zeolites. This flexibility enables a dynamic behavior in porous coordination networks, which facilitate structural modifications (guest exchange or chemical reactions within the pores) without loss of its structural integrity. Hence, chemical reactions that occur in the pore can be monitored *in situ* in great detail by X-ray crystallography and other spectroscopic techniques.

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The growing interest in such materials both scientifically and economically is not surprising due to the remarkable physicochemical properties that have been reported during the last two decades. Organic coordination networks are useful in a wide range of applications. For instance, these porous networks can be used in processes such as selective separation, catalytic reactions, guest exchange, and gas storage. Thus, due to its importance, in this review we have summarized the history of the coordination networks from the first documented examples until the latest advances in this field.

1.2 DISCOVERY OF A COORDINATION NETWORK

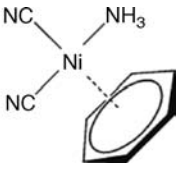
Initially porous and open-framework coordination networks attracted considerable attention as post-zeolite materials. Recent progresses of coordination networks are remarkable in that many intriguing properties and functions, for example robust and flexible framework, framework transformation, pore post-modification, selective molecular recognition, gas adsorption, and catalysis, have been reported. This review follows the history of coordination networks from the beginning, namely, Hofmann complex.

1.2.1 Hofmann Complex

The first coordination network having a chemical formula of $Ni(CN)_2(NH_3)\cdot C_6H_6$ was discovered by Hofmann and Küspert in 1897.[1] They obtained the complex as a crystal by slow layering diffusion of C_6H_6 into an NH_3 solution of $Ni(CN)_2$. Pfeiffer in 1927[2] and Feigl in 1944[3] speculated that the structure of Hofmann complex was a Ni monomer coordinated by benzene as a side-on form, $Ni(CN)_2(NH_3)(\eta^6\text{-}C_6H_6)$ (Scheme 1.1).

Finally in 1954 Powell and coworkers clarified the structure of the Hofmann complex by X-ray analysis (unit cell dimensions $a = b = 7.242$ Å; $c = 8.277$ Å^3; $\alpha = \beta = \gamma = 90$). The crystal structure was a square network bridged by CN groups encapsulating benzene in a channel.[4] A partial structure of the Hofmann complex is shown in Figure 1.1. Arrays of Ni covalently linked through CN groups form two-dimensional layers that are parallel to each other. From each layer two amine groups protrude toward the adjacent layer, creating a series of voids where benzene molecules are included.

Speculation:



SCHEME 1.1

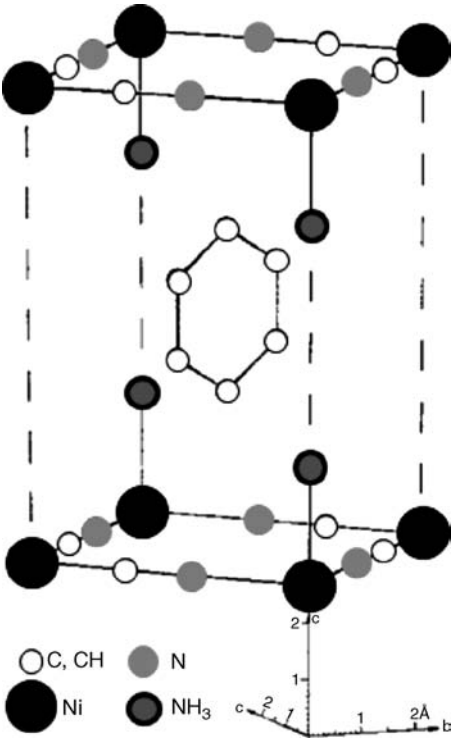


FIGURE 1.1 A partial crystal structure of the Hoffman complex showing benzene encapsulation within the cavity.

1.2.2 Variation of the Hofmann Complex

Thereafter various Hofmann type complexes have been reported. Iwamoto and coworkers reported $M^1M^2(NH_3)_2(CN)_4 \times \mathbf{G}$ (M^1: Ni, Zn, Cd, Cu, Mn, Fe, Co; M^2: Ni, Pd, Pt; **G**: benzene, aniline, pyrrole, thiophene) in 1967–1968.[5,6] They paid attention to the components of Hofmann complex that can be divided into three parts: $[Ni(NH_3)_2]^{2+} + [Ni(CN)_4]^{2-} + 2C_6H_6$. Therefore, they prepared Hofmann type complexes according to the following Scheme 1.2. The structures were identified by powder X-ray diffraction analysis.

Walker and Hawthorne proposed expanded *n*-alkylamine Hofmann complexes in 1966 (Figure 1.2).[7] The complexes were synthesized by addition of *n*-alkylamines to a suspension to anhydrous nickel cyanide (Scheme 1.3). The crystalline samples were studied using the powder X-ray diffraction technique.

$$[M^1(NH_3)_2]^{2+} + [M^2(CN)_4]^{2-} \xrightarrow{\mathbf{G}} M^1M^2(NH_3)_2(CN)_4 \cdot 2\mathbf{G}$$

SCHEME 1.2

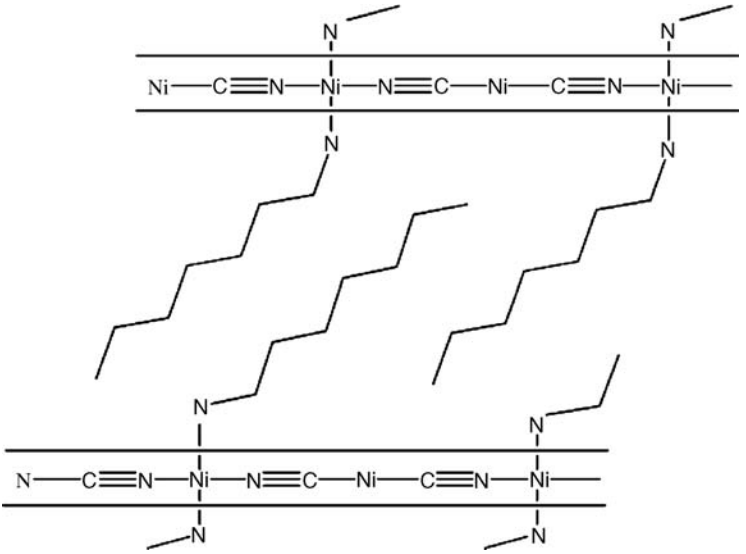


FIGURE 1.2 Proposed structure of the expanded Hofmann complexes using *n*-alkylamines.

In 1968–1975, Iwamoto and coworkers also reported expanded Hofmann complexes bridged by ethylenediamine (en)[8] (Scheme 1.4). The structure was determined by X-ray analysis (Figure 1.3). The coordination network can encapsulate aromatic guests such as aniline, benzene, thiophene, and pyrrole.

In 1977, Mathey prepared aromatic diamine complexes as shown in Scheme 1.5.[9] Depending on the length of diamines, the length of the *c*-axis also varies (Figure 1.4). The diamine complexes show selective encapsulation for aromatic guests and solvents. For example, [Ni(4,4′-bipyridyl)$Ni(CN)_4$] encapsulate 0.8G (G: benzene, naphthalene, anthracene, $CHCl_3$, CH_2Cl_2, CH_3OH, but not phenanthrene, CCl_4).

$$Ni(CN)_2 + n\text{-alkylamine} \longrightarrow Ni(CN)_2 \cdot n\text{-alkylamine}$$

SCHEME 1.3

$$CdCl_2 + K_2M(CN)_4 + en \longrightarrow [Cd(en)M(CN)_4] \cdot 2C_6H_6$$

SCHEME 1.4

$$Ni(CN)_2 + \text{diamine} \xrightarrow[24\ h]{110^\circ C} Ni(CN)_2(\text{diamine})$$

SCHEME 1.5

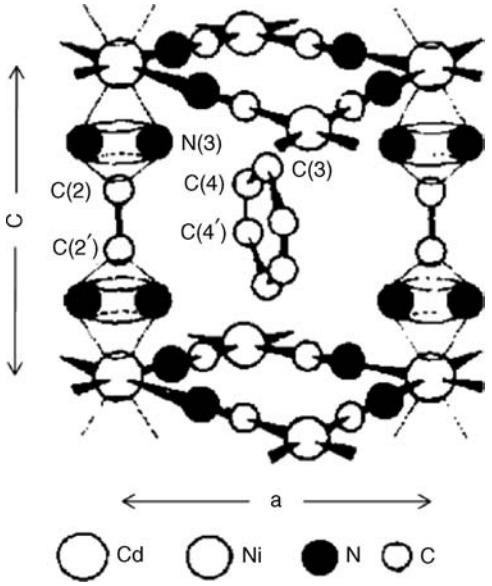


FIGURE 1.3 Representation of $[Cd(en)Ni(CN)_4]\cdot 2C_6H_6$.

Likewise Iwamoto and coworkers expanded from Hofmann complex into 1,2-diaminopropane (pn) complex in 1980,[10] dimethylamine complex in 1982–1984,[11] and 1,ω-diaminoalkane complex (1,ω-diaminoalkane: $H_2N(CH_2)_nNH_2$, $n = 4$–8) in 1984–1985.[12] Each complex encapsulated specific aromatic compounds. In addition, they prepared many related complexes by combination of metal ions with bridging ligands.[13]

As a whole, Iwamoto and colleagues developed unique chemistry of intriguing series of Hofmann complexes. He is one of pioneers to show promising future visions of designable coordination networks as a new class of materials.

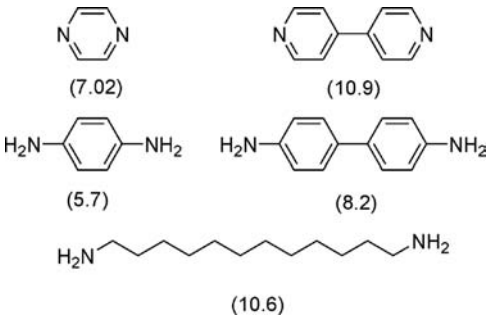


FIGURE 1.4 Diamines and *c*-axis values (in parentheses, Å).

1.3 ORGANIC COORDINATION NETWORK: ORGANIC MODIFICATION OF THE HOFMANN COMPLEX

Hofmann complex inspired scientists to develop strategies aiming to find a new class of materials. Worldwide the effort of many researchers paved the way for finding a new route to synthesize materials having larger cavities. For instance, if a –CN group could be replaced with organic linkers, a variety of coordination networks having finely tuned cavities could be prepared.

1.3.1 Organic Coordination Network: The First Example

In 1989, Robson reported the first organic coordination network by complexation of anions with tetrahedral bridging ligands.[14] The aim of their work was to prepare three-dimensional solid polymeric materials with cavities by linking centers together with either a tetrahedral or an octahedral array of valencies. They prepared an infinite framework $\{Cu^{I}[C(C_6H_4{\cdot}CN_4)]\}^+$ of tetrahedral centers linked together by rod-like units. The rod-like units were obtained by substitution of the acetonitrile ligands in $[Cu^{I}(CH_3CN)_4]^+$ by 4,4′,4″,4-tetracyanotetraphenylmethane.

X-ray crystallographic analysis revealed a diamond-like structure containing disordered nitrobenzene and BF_4^- ions in the cavities (Figure 1.5). The framework has adamantane-like cavities with a volume of approximately 700 $Å^3$. It was estimated

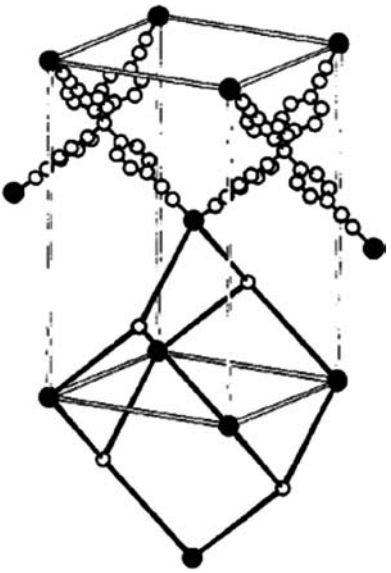


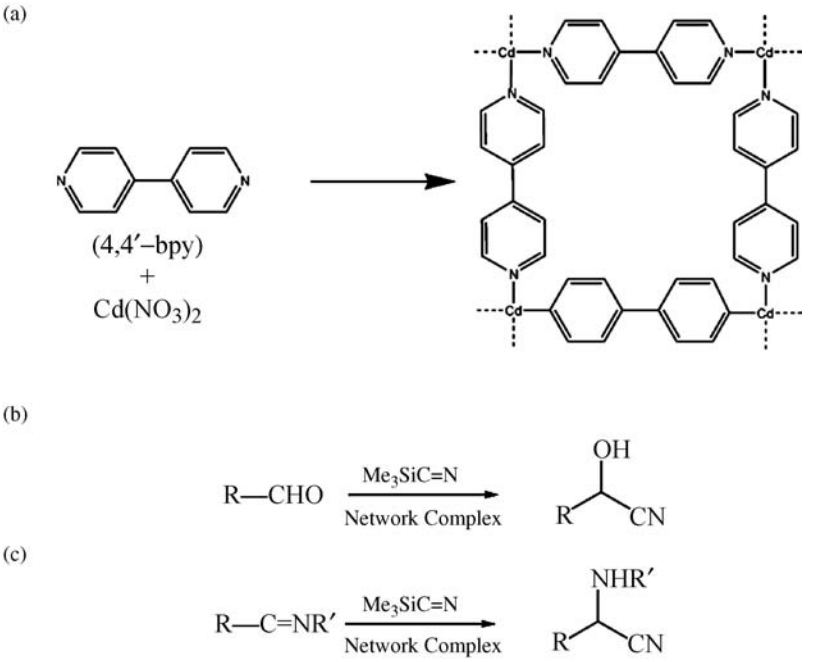
FIGURE 1.5 Tetragonal unit cell with parts of adjacent unit cells of $\{Cu^{I}[C(C_6H_4{\cdot}CN_4)]\}^+$. Gray circles denote the Cu atoms. The adamantane-like cavity is highlighted (black sticks). Nitrobenzene molecules and BF_4^- are omitted for clarity.

that the framework represents one third of the volume of the crystal while the remaining two thirds correspond to the nitrobenzene and BF_4^- ions.

With this work Robson and coworkers established a new strategy capable of designing new solids containing large cavities by linking organic molecules with determined size and shape.

1.4 M-BIPYRIDINE SQUARE GRIDS: TWO-WAY LINK. TOWARD NEW FUNCTIONS AND APPLICATIONS OF ORGANIC COORDINATION NETWORKS

The preparation of a macrocyclic polynuclear complex $[(en)Pd(4,4'\text{-bpy})]_4(NO_3)_8$ (bpy = bipyridine) with the ability to recognize organic molecules in aqueous environment was an important step toward the applicability of such organic coordination networks.[15] Such applicability was demonstrated in 1994 with the synthesis of a two-dimensional square network solid $[Cd(4,4'\text{-bpy})_2(NO_3)_2]$ containing large cavities with the possibility of guest encapsulation (Scheme 1.6a).[16] Crucially, the first catalytic process within a porous coordination network was demonstrated by treating benzaldehyde and cyanotrimethylsilane with a CH_2Cl_2 suspension of powdered $[Cd(4,4'\text{-bpy})_2(NO_3)_2]$ (40°C, 24 h), which gave 2-(trimethylsiloxy)phenylacetonitrile) in 77% yield (Scheme 1.6b). Later on, we reported the cyanosilylation of imines catalyzed by $[Cd(4,4'\text{-bpy})_2(H_2O)_2](NO_3)_2{\cdot}4H_2O$ (Scheme 1.6c).[17]



SCHEME 1.6

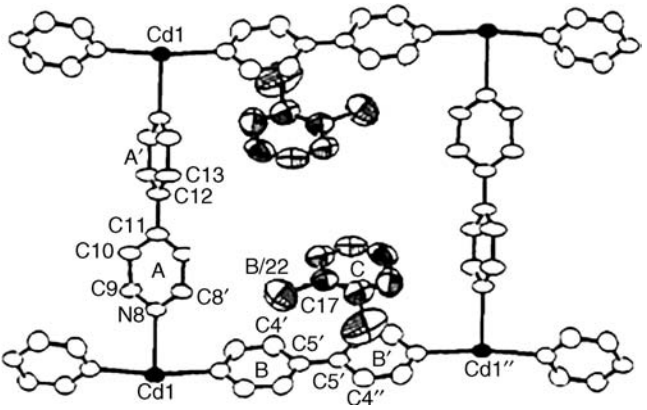


FIGURE 1.6 View of the complex $[Cd(bpy)_2](NO_3)_2(C_6H_4Br_2)_2$ showing 50% probability ellipsoids. Nitrate ions have been omitted for clarity.

The ability to include guest molecules within the cavities was observed by preparation of a clathrate with *o*-dibromobenzene. The inclusion of the aromatic guest was confirmed by single-crystal X-ray diffraction. The structure was described as a graphite-like stacking of two-dimensional layers on top of each other (i.e., interplanar distance *ca.* 6.30 Å). One layer consists of an edge-sharing, perfectly planar square with a Cd(II) ion and 4,4′-bpy at each corner and side, respectively. Two *o*-dibromobenzene are included in each square void (Figure 1.6).

At the almost same time, Zaworotko and Yaghi reported organic coordination networks in 1995.[18,19] Zaworotko and coworkers reported the formation of a coordination network $[Zn(4,4'\text{-bpy})_2]SiF_6$ with large non-interpenetrated channels (Figure 1.7). The effective pore size (8×8 Å^2) is comparable to the pore sizes of

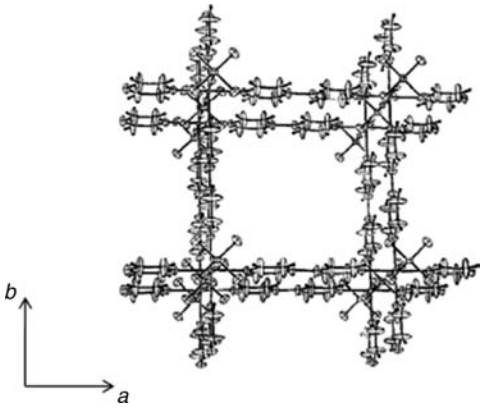


FIGURE 1.7 ORTEP representation of a square channel viewed along the *c* crystallographic axis. The dimensions of the channels are the same as the dimensions of the unit cell *ca.* 11.396×11.396 Å^2.

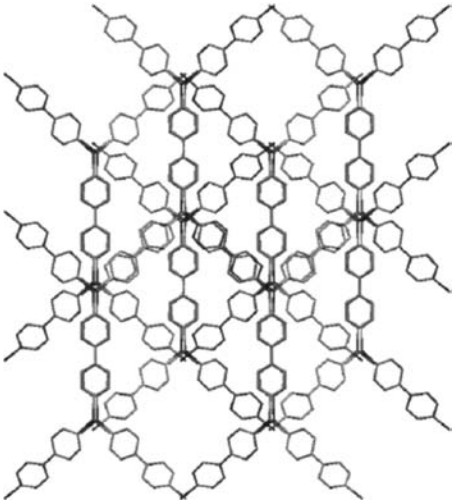


FIGURE 1.8 Crystal structure of $[Cu(4,4'\text{-bpy})_{1.5}](NO_3)\cdot(H_2O)_{1.25}$ viewed along the [100] crystallographic direction. Nitrate anions and water molecules have been omitted for clarity.

large zeolites. The volume corresponding to the pores is about the 50% of the total volume. Interestingly, the pores are hydrophobic, which, in principle, should be able to include hydrophobic molecules with dimensions in the order of the pore size.

In the same year, Yaghi and coworkers succeeded on the hydrothermal synthesis preparation of another coordination network containing three identical interpenetrated channels. Single-crystal X-ray diffraction revealed the extended network of $[Cu(4,4'\text{-bpy})_{1.5}]NO_3\,(H_2O)_{1.25}$ in which trigonal planar Cu^{I} centers are linked by rod-like 4,4′-bpy ligands forming an extended 3D porous network (Figure 1.8). The interpenetrated networks did not fill all the available space as observed in many other solids, therefore leaving an important volume of the solid as rectangular channels. Those channels are filled with nitrate anions and water molecules and are linked by hydrogen bond interactions. Ion exchange properties were investigated. Nitrate ions were replaced in aqueous solutions with other ions such as SO_4^{2-} and BF_4^{-}. Under inert atmosphere, the coordination network was observed to be stable up to 180°C and for hours in water at 70°C.

The synthesis and crystal structures of new porous coordination networks with gas adsorption properties were first reported by Kitagawa and coworkers in the late 1990s.[20] Three structures $[M_2(4,4'\text{-bpy})_3(NO_3)_4](H_2O)_x$ (where M = Co, Ni, and Zn) were characterized by X-ray crystallography. The coordination network with Co metal was determined by single-crystal X-ray diffraction, and the isomorphous porous coordination networks with Ni and Zn metals were demonstrated by powder X-ray diffraction (Figure 1.9). These solids have two channels running parallel to the *b* and *c* crystallographic axes whose dimensions are 3×6 and 3×3 Å^2, respectively. The channels are filled with water molecules that are not bonded to the crystal framework.

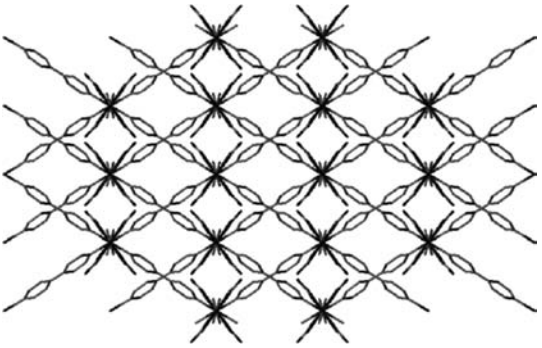


FIGURE 1.9 Crystal structure corresponding to $[Co_2(4,4'\text{-bpy})_3](NO_3)_4\cdot(H_2O)_4$ viewed along the *c*-axis. Hydrogen atoms have been omitted for clarity.

Gas-adsorption properties were studied due to the 3D porous nature of such coordination network. Under dried vacuum, the adsorption activity for CH_4, N_2, and O_2 was investigated. Clearly, diffusion of the different gases was observed (Figure 1.10). For 1 g of the anhydrous sample at 30 atm, about 2.3 mmol of CH_4 and 0.80 mmol of N_2 or O_2 were adsorbed. Importantly, powder X-ray diffraction confirmed that during the gas adsorption process there was no loss of crystallinity.

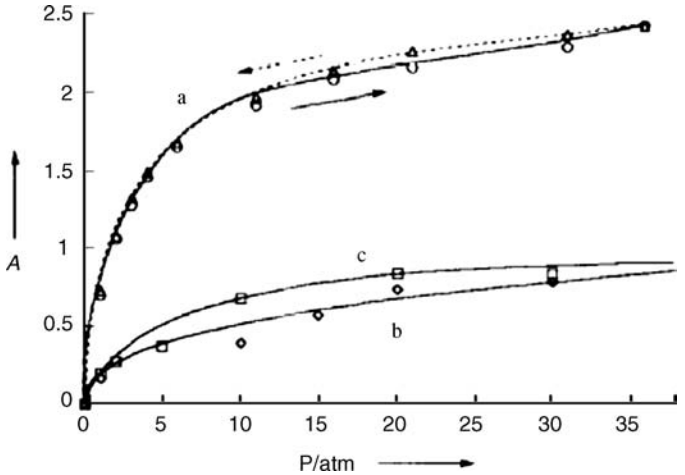


FIGURE 1.10 Isotherms showing the adsorption of CH_4 (a), N_2 (b), and O_2 (c) carried at room temperature for $[Co_2(4,4'\text{-bpy})_3](NO_3)_4\cdot(H_2O)_4$ in the range of 1–36 atm. For the CH_4 gas desorption (circles) was carried out directly after gas adsorption (triangles). The similarity between the two curves denotes that there are no structural changes during the adsorption process.

1.5 SINGLE-CRYSTAL-TO-SINGLE-CRYSTAL PHENOMENA IN POROUS COORDINATION NETWORKS

After application to catalysis, our interests moved on to single-crystal-to-single-crystal phenomena (SCSC), because organic coordination networks often crystallize very well. Crystallographic studies are useful as they provide valuable information about the relative atomic and molecular positions within a crystalline solid. In this regard, detailed information can be obtained from SCSC transformations. For instance, such solid-state processes enable one to analyze framework transformations and molecular interactions between guest–guest and host–guest within the pores in detail.[21]

1.5.1 SCSC Guest Removal

The first successful SCSC guest removal was reported by Kepert in 2000.[22] They prepared $[Ni_2(4,4'\text{-bpy})_3](NO_3)_4{\cdot}6EtOH$. The interlocked bilayer framework has 6×3 Å^2 channels, which can reversibly uptake H_2O at room temperature with other guests such as EtOH, MeOH, and *i*-PrOH (Figure 1.11). The desolvation process at 100°C causes just a 2.4% decrease in cell volume and the mosaicity of the crystal remains intact.

1.5.2 SCSC Framework Dynamics

Unlike zeolite, one of salient features of organic coordination networks is their flexible frameworks capable of SCSC drastic framework transformation. We reported in 2000 the synthesis of an open 20×20 Å^2 square-grid coordination network. [Ni(4,4′-bis(4-pyridyl)biphenyl)$_2$]$(NO_3)_2{\cdot}4$(*o*-xylene) was prepared via self-assembly of a rod-like ligand, 4,4′-bis(4-pyridyl)biphenyl, with $Ni(NO_3)_2$ in *o*-xylene.[23] The framework has remarkable thermal stability and maintains its integrity up to 300°C. SCSC sliding of 2D-coordination layers of [Ni(4,4′-bis(4-pyridyl)biphenyl)$_2$]$(NO_3)_2{\cdot}4$(*o*-xylene)[24] triggered by guest exchange was successfully observed by X-ray analysis (Figure 1.12).[25] The crystals of [Ni(4,4′-bis(4-pyridyl)biphenyl)$_2$]$(NO_3)_2{\cdot}4$(*o*-xylene) showed guest specificity and exchanges of *o*-xylene for mesitylene but not for *m*-xylene, or 1,3- or 1,2-dimethoxybenzene. The crystals of a mesitylene-inclusion network, [Ni(4,4′-bis(4-pyridyl)biphenyl)$_2$]$(NO_3)_2{\cdot}1.7$(mesitylene), were prepared by immersion of [Ni(4,4′-bis(4-pyridyl)biphenyl)$_2$]$(NO_3)_2{\cdot}4$(*o*-xylene) in mesitylene for 6 h. The single-crystal analysis of [Ni(4,4′-bis(4-pyridyl)biphenyl)$_2$]$(NO_3)_2{\cdot}1.7$-(mesitylene) revealed considerable sliding of the layers relative to the 2D-framework of [Ni(4,4′-bis(4-pyridyl)biphenyl)$_2$]$(NO_3)_2{\cdot}4$(*o*-xylene) (Figure 1.13). Edge-to-face aromatic interactions exist at the corner of the channels in both [Ni(4,4′-bis(4-pyridyl)-biphenyl)$_2$]$(NO_3)_2{\cdot}4$(*o*-xylene) and [Ni(4,4′-bis(4-pyridyl)biphenyl)$_2$]$(NO_3)_2{\cdot}1.7$-(mesitylene) but not along the walls. The dimensions of the channels in [Ni(4,4′-bis(4-pyridyl)biphenyl)$_2$]$(NO_3)_2{\cdot}1.7$(mesitylene) are much bigger than those of [Ni(4,4′-bis(4-pyridyl)biphenyl)$_2$]$(NO_3)_2{\cdot}4$(*o*-xylene). The sliding motion of the 2D-layers could be monitored by X-ray powder and single-crystal diffraction. The crystallographic results and GC analysis clearly indicate that the framework

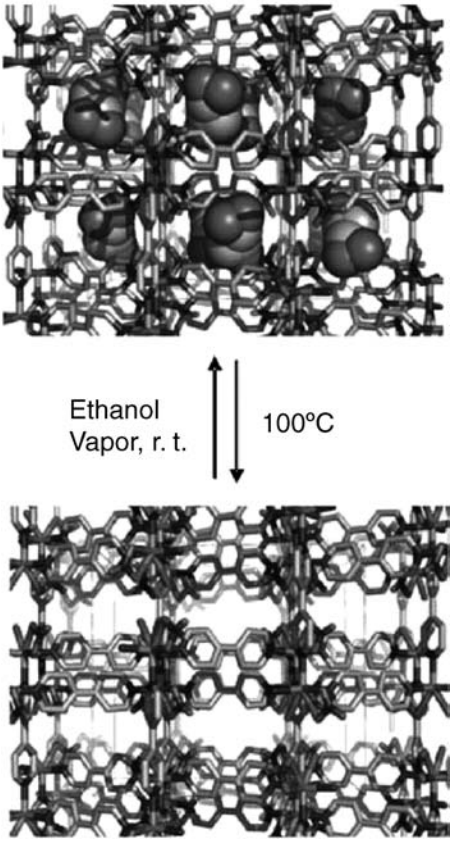


FIGURE 1.11 Guest inclusion/removal in $[Ni_2(4,4'\text{-bpy})_3](NO_3)_4 \cdot 6EtOH$ viewed down the *a*-axis. Ethanol molecules (space-filling model) are disordered.

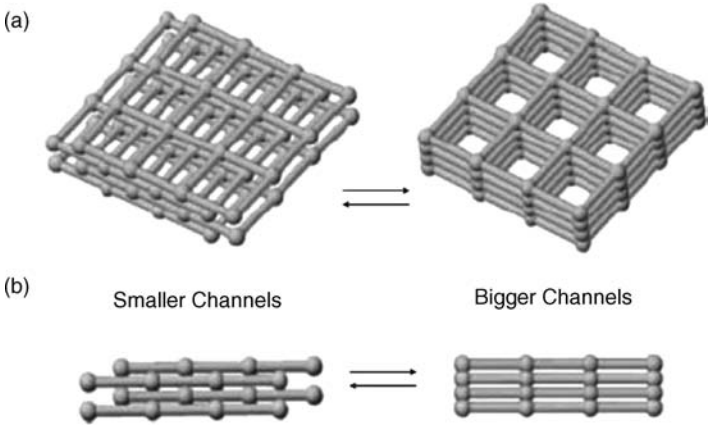


FIGURE 1.12 Sliding motion of 2D-layers: (a) top and (b) side views.

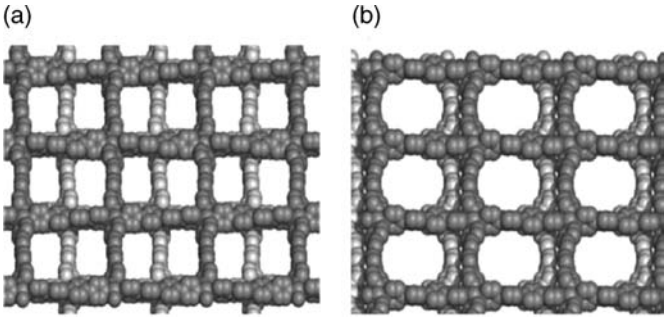


FIGURE 1.13 Packing of 2D layers viewed along the *c*-axis in (a) [Ni(4,4′-bis(4-pyridyl)-biphenyl)$_2$](NO$_3$)$_2$·4(*o*-xylene) 4 and (b) Ni(4,4′-bis(4-pyridyl)biphenyl)$_2$](NO$_3$)$_2$·1.7(mesitylene). Solvent molecules are omitted for clarity.

transformation proceeds in a crystal-to-crystal fashion. The first step is guest exchange, and the second step is the sliding of the layers.

Two years later, in 2002, Suh and coworkers also reported SCSC dynamic framework transformation.[26] They prepared a coordination porous bilayer-open-framework (BOF-1), $[Ni_2(C_{26}H_{52}N_{10})]_3[BTC]_4{\cdot}6C_5H_5N{\cdot}36H_2O$, which was synthesized from the reaction of dinickel(II) bismacrocyclic complex $[Ni_2(C_{26}H_{52}N_{10})(Cl)_4]{\cdot}H_2O$ and sodium 1,3,5-benzenetricarboxylate (Na_3BTC) in water in the presence of DMSO and pyridine.

X-ray diffraction revealed two-dimensional layers formed between the Ni(II) macrocyclic unit and the BTC^{3-} ions are separated by the *p*-xylyl groups that act as pillars (Figure 1.14).

The coordination network has 3D channels with an effective channel width of *ca.* 11.12 Å (Figure 1.14 top) that are filled with water and pyridine molecules. The void volume corresponding to the channels was estimated to be 61% of the total volume. Upon exposure of $[Ni_2(C_{26}H_{52}N_{10})]_3[BTC]_4{\cdot}6C_5H_5N{\cdot}36H_2O$ at 75°C for 1.5 h, all the aromatic and nearly all water molecules were removed to yield $[Ni_2(C_{26}H_{52}N_{10})]_3[BTC]_4{\cdot}4H_2O$. Despite the significant structural reorganization (i.e., the cell volume changed from 5974.3 to 3877.9 Å^3) the crystallinity was maintained. It was observed by X-ray diffraction that the thickness of the bilayer was reduced considerably due to the tilting of the *p*-xylyl molecules (Figure 1.14 bottom). Interestingly, powder X-ray diffraction revealed that the process is reversible when $[Ni_2(C_{26}H_{52}N_{10})]_3[BTC]_4{\cdot}4H_2O$ was immersed in a solution containing water and pyridine during only 5 min.

1.5.3 Robust Hydrogen-Bonded 2D-Grid Network

In 2005, we reported a robust 2D-grid network considerably stabilized by hydrogen bonding.[27] The bidentate bridging ligand was simply modified by introducing ethylene glycol chains as hydrogen bonding sites. The modification of the link enabled us to perform the *in situ* crystallographic observation of reversible apical ligand

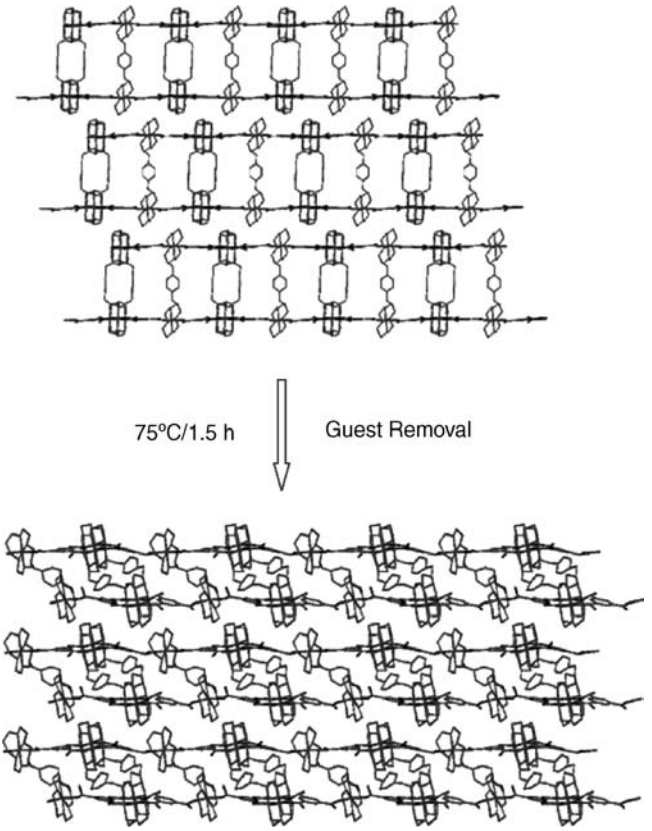
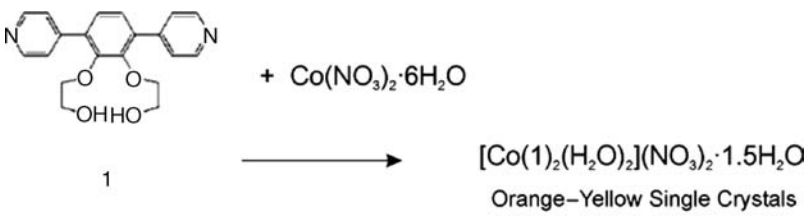


FIGURE 1.14 X-ray structures of BOF-1. View of $[Ni_2(C_{26}H_{52}N_{10})]_3[BTC]_4 \cdot 6C_5H_5N \cdot 36H_2O$ along the *a*-axis (top). View along the *b*-axis of $[Ni_2(C_{26}H_{52}N_{10})]_3[BTC]_4 \cdot 4H_2O$ showing the tilting of the *p*-xylyl groups as a consequence of the water loss (bottom). Water and pyridine molecules have been omitted for clarity.

exchange at a cobalt center at 150°C. It was shown how the aqua and nitrate ligands can be reversibly coordinated to the cobalt center in a SCSC fashion.

A rod-like pyridyl ligand containing ethylene glycol side chains (**1**) was synthesized (Scheme 1.7). Slow complexation of $Co(NO_3)_2 \cdot 6H_2O$ in MeOH over a solution



1

2

SCHEME 1.7

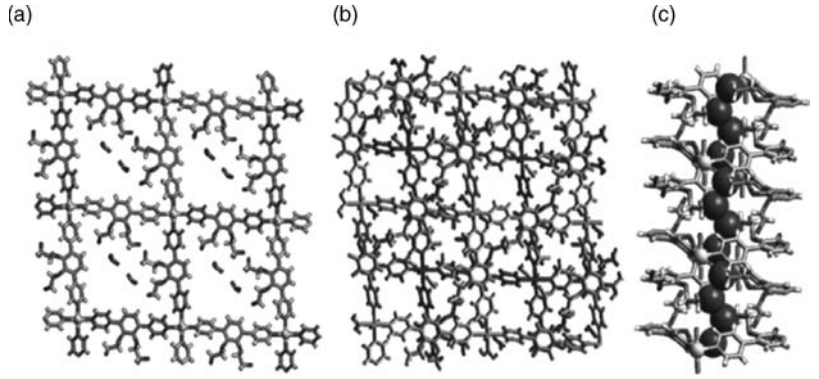


FIGURE 1.15 (a) Square-rigid network of $[Co(\mathbf{1})_2(H_2O)_2](NO_3)_2{\cdot}1.5H_2O$. Guest molecules ($H_2O$) have been omitted for clarity. (b) The two-layer stack of **2**. (c) The infinite 1D hydrogen bonding interaction (O–H $\cdots$ O) between layers in $[Co(\mathbf{1})_2(H_2O)_2](NO_3)_2{\cdot}1.5H_2O$. The oxygen atoms of the hydroxyl groups are represented by a space-filling model.

of **1** in toluene produced orange–yellow single crystals of $[Co(\mathbf{1})_2(H_2O)_2](NO_3)_2{\cdot}1.5H_2O$ (**2**).

Crystallographic analysis revealed the formation of square-grid network structure where the grid sheet layers are stacked on top of each other (Figure 1.15a). The two layers are in an offset fashion on both edges (Figure 1.15b). Interestingly, the ethylene glycol chains play two important roles. First, they add considerable stabilization to the crystal due to 1D hydrogen-bond (O–H $\cdots$ O) arrays that interpenetrate the layers (Figure 1.15c). Second, they also introduce moderate flexibility within the cavity by allowing guest molecules to behave as in a solution-like environment. In fact, a similar square-grid coordination network without functionalized bridging ligands gradually deteriorated above room temperature due to the loss of guest molecules. Importantly, the increased stability and flexibility of $[Co(\mathbf{1})_2(H_2O)_2](NO_3)_2{\cdot}1.5H_2O$ allowed us to directly observe a reversible apical-ligand-exchange reaction at the hinge metals by single-crystal X-ray crystallography.

Two water molecules are coordinated to the cobalt(II) center at the apical positions (aqua form) with four pyridyl groups at the equatorial positions (Figure 1.16a). Upon heating at 150°C a single crystal of $[Co(\mathbf{1})_2(H_2O)_2](NO_3)_2{\cdot}1.5H_2O$ during 1 day, the yellow crystal turned red without loss of crystallinity. Crystallographic analysis revealed that the apical water molecules were substituted by two nitrate ions and extruded from the crystal to form the nitrate complex $[Co^{II}(\mathbf{1})_2(NO_3)_2]$ (Figure 1.16b). It was observed that after leaving $[Co^{II}(\mathbf{1})_2(NO_3)_2]$ at room temperature, it returned to the initial aqua form. The crystal changed from red to yellow in color and the crystallinity was maintained. Crystallographic and elemental analysis showed that the new obtained aqua form $[Co(\mathbf{1})_2(H_2O)_2](NO_3)_2{\cdot}1.5H_2O$ is almost identical to the original structure of $[Co(\mathbf{1})_2(H_2O)_2](NO_3)_2{\cdot}1.5H_2O$ (Figure 1.16c).

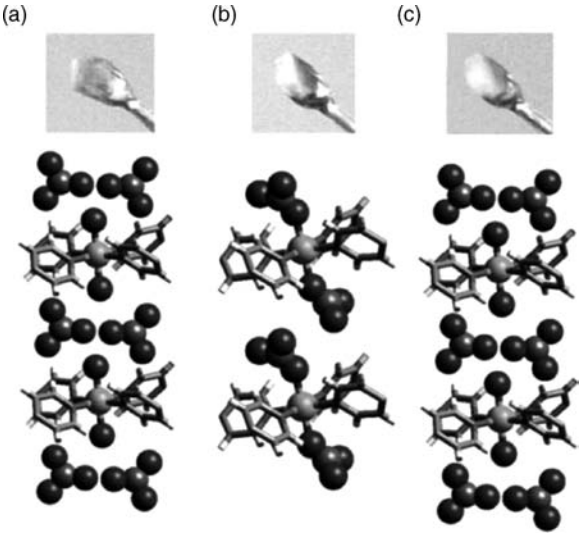


FIGURE 1.16 Photographs corresponding to the actual crystals and molecular structures around the cobalt ion: (a) original crystal $[Co(\mathbf{1})_2(H_2O)_2](NO_3)_2{\cdot}1.5H_2O$, (b) the crystal after heating at 150°C for 24 h $[Co^{II}(\mathbf{1})_2(NO_3)_2]$, and (c) the crystal after exposure of $[Co^{II}(\mathbf{1})_2(NO_3)_2]$ to air $[Co(\mathbf{1})_2(H_2O)]_2(NO_3)_2{\cdot}1.5H_2O$. Two other disordered nitrate ions have been omitted for clarity.

1.6 EXPANSION FROM TWO- TO THREE-WAY LINK: CONSTRUCTION OF TPT COORDINATION NETWORKS

Self-assembly of a two-way link with metal ion connectors provides predictable architecture. What about a three-way link? The triazine ligand 2,4,6-tris(4-pyridyl)-triazine (TPT) was chosen as a three-way link. In fact, a three-way link of TPT gives more variety of discrete coordination cages having a large void capable of encapsulating hydrophobic guests. We reported molecular M_6L_4 cages (M: *cis*-protected Pd or Pt; L: TPT) in 1995.[28] Meanwhile we attempted to prepare coordination networks consisting of metal ions and TPT, but had no success.

In 1996, Robson and coworkers succeeded in the preparation of a TPT coordination network.[29] A porous coordination network in which two independent cubic nets are interpenetrated was synthesized by diffusion of a solution of $[Cu(CH_3CN_4)]ClO_4$ in acetonitrile into a solution of TPT in $CHCl_3$/1,1,2,2-tetrachloroethane. Dark red crystals of $[Cu_3(TPT)_4](ClO_4)_3$ were analyzed by single-crystal X-ray diffraction.

The repeating structural unit in the network is formed by six Cu centers at the corners of a regular octahedron. Large octahedral chambers are formed in which each chamber is connected through six Cu metal vertices to six others (Figure 1.17). An infinite arrangement of cubic chambers is then produced. At the center of each collection of eight chambers, there is a cavity that can accommodate a chamber of an independent but identical infinite network (Figure 1.18). Importantly, the octahedral chambers are left unoccupied, which generates a solid with large empty voids that can include other molecules.