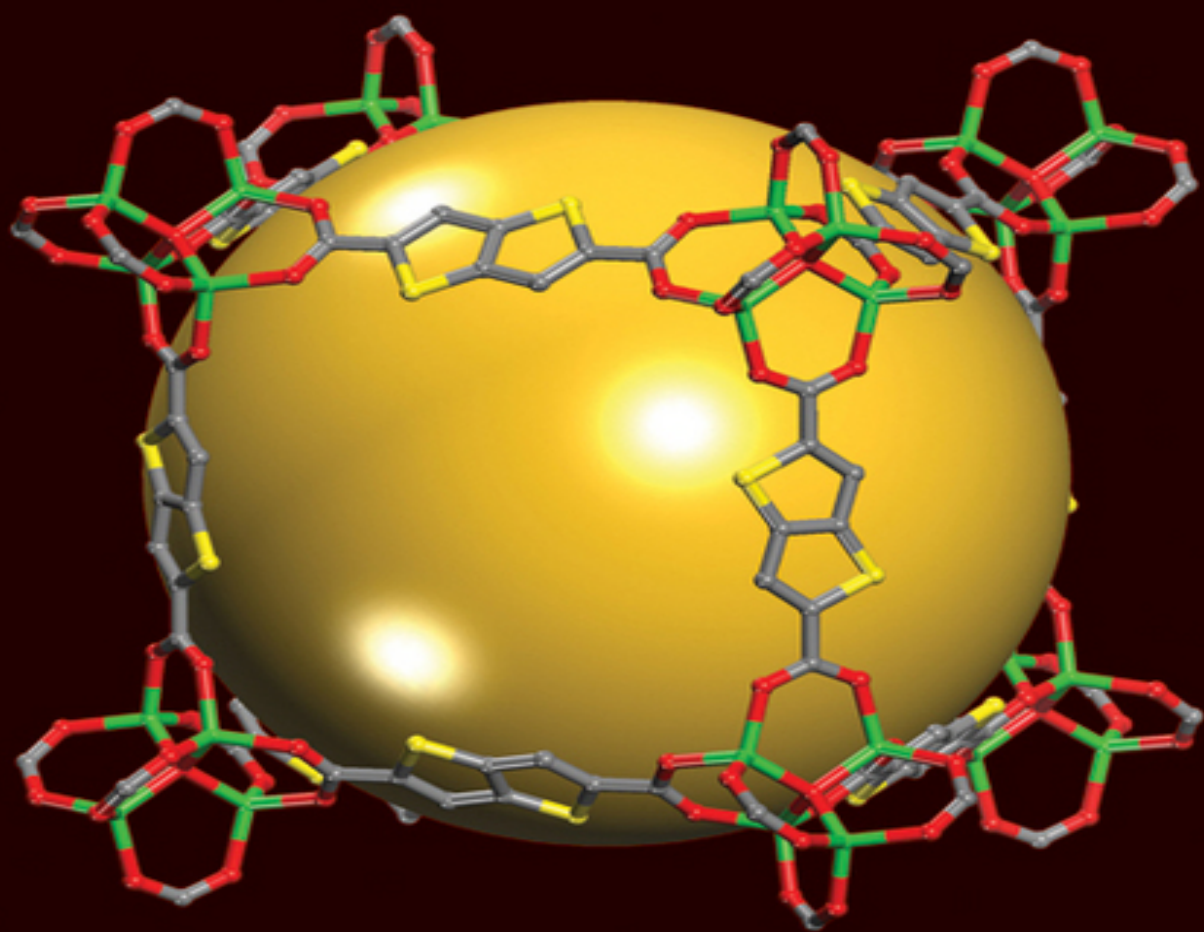


Metal-Organic Frameworks

Design and Application

Edited by Leonard R. MacGillivray



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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., H₂) 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

Reference

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

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Chapter 1

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.

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

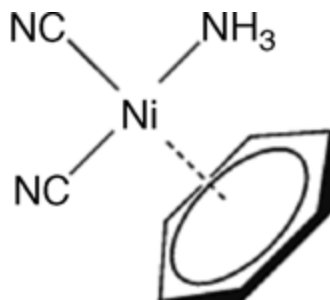
history of coordination networks from the beginning, namely, Hofmann complex.

1.2.1 Hofmann Complex

The first coordination network having a chemical formula of $\text{Ni}(\text{CN})_2(\text{NH}_3)\cdot\text{C}_6\text{H}_6$ 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 $\text{Ni}(\text{CN})_2$. 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, $\text{Ni}(\text{CN})_2(\text{NH}_3)(\eta^6\text{-C}_6\text{H}_6)$ ([Scheme 1.1](#)).

[Scheme 1.1](#)

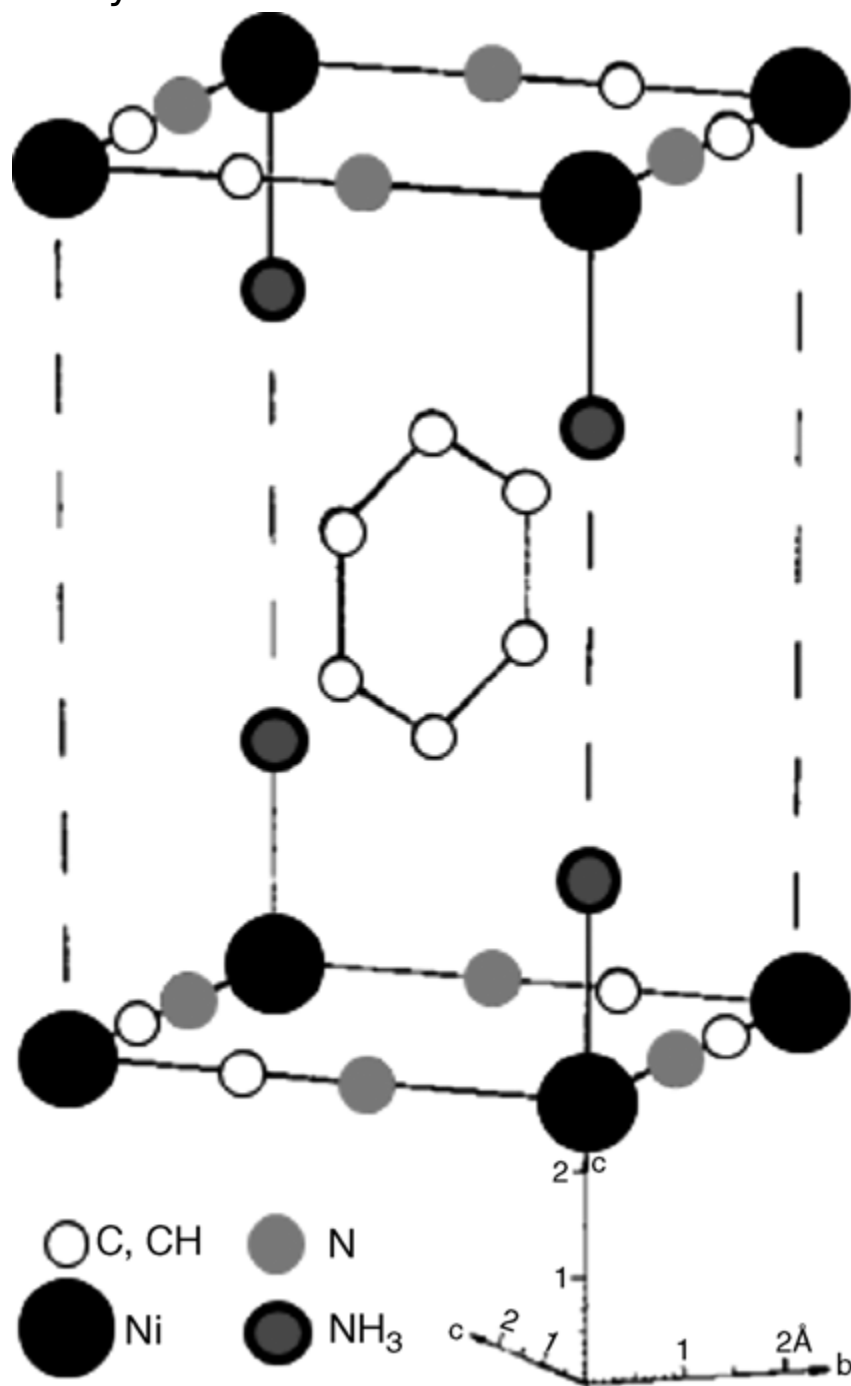
Speculation:



Finally in 1954 Powell and coworkers clarified the structure of the Hofmann complex by X-ray analysis (unit cell dimensions $a = b = 7.242 \text{ \AA}$; $c = 8.277 \text{ \AA}^3$; $\alpha = \beta = \gamma = 90$). 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.

[Figure 1.1](#) A partial crystal structure of the Hoffman complex showing benzene encapsulation within the

cavity.

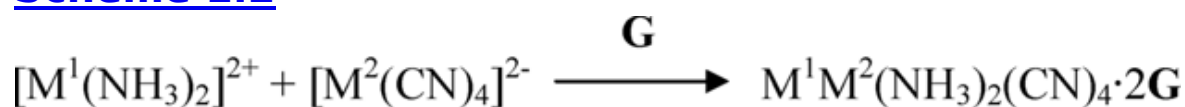


1.2.2 Variation of the Hofmann Complex

Thereafter various Hofmann type complexes have been reported. Iwamoto and coworkers reported

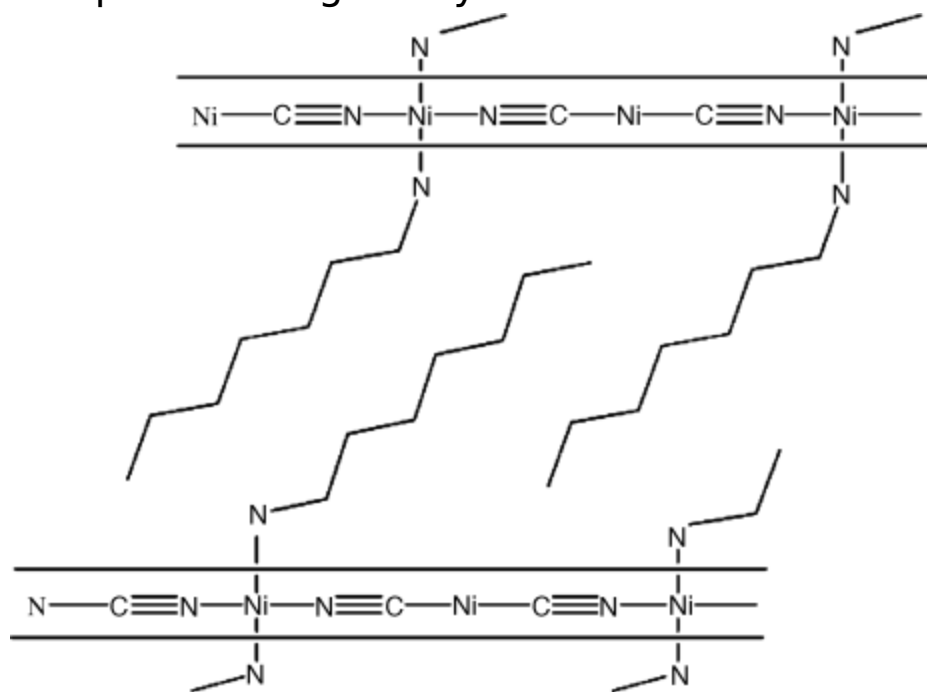
$M^1M^2(NH_3)_2(CN)_4 \times G$ (M^1 : Ni, Zn, Cd, Cu, Mn, Fe, Co; M^2 : Ni, Pd, Pt; G : benzene, aniline, pyrrole, thiophene) in 1967-1968. [5, 6] They paid attention to the components of Hofmann complex that can be divided into three parts: $[Ni(NH_3)_2]^{2+} + [Ni(CN)_4]^{2-} + 2C_6H_6$. Therefore,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

Scheme 1.2

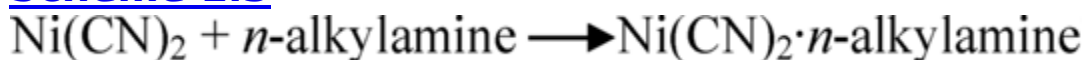


Walker and Hawthorne proposed expanded *n*-alkylamine Hofmann complexes in 1966 ([Figure 1.2](#)). [7] The complexes were synthesized by addition of *n*-alkylamines to a suspension to anhydrous nickel cyanide ([Scheme 1.3](#)). The crystalline samples were studied using the powder X-ray diffraction technique.

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

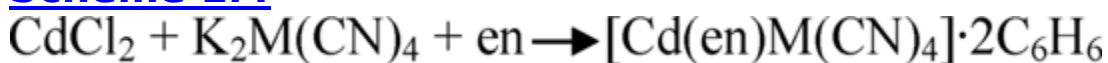


Scheme 1.3

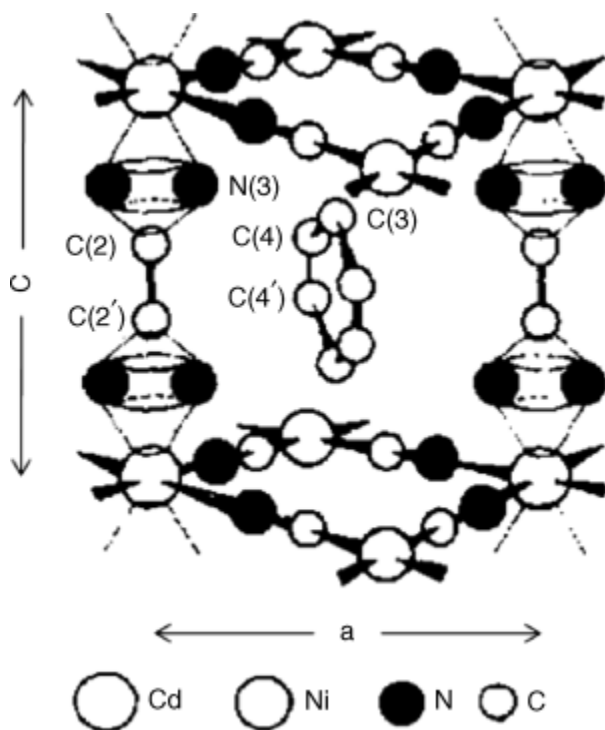


In 1968–1975, Iwamoto and coworkers also reported expanded Hofmann complexes bridged by ethylenediamine (en) [8] ([Scheme 1.4](#)). The structure was determined by X-ray analysis ([Figure 1.3](#)). The coordination network can encapsulate aromatic guests such as aniline, benzene, thiophene, and pyrrole.

Scheme 1.4



[Figure 1.3](#) Representation of $[\text{Cd}(\text{en})\text{Ni}(\text{CN})_4] \cdot 2\text{C}_6\text{H}_6$.



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, $[\text{Ni}(4,4'\text{-bipyridyl})\text{Ni}(\text{CN})_4]$ encapsulate 0.8G (G: benzene,

naphthalene, anthracene, CHCl_3 , CH_2Cl_2 , CH_3OH , but not phenanthrene, CCl_4).

Scheme 1.5

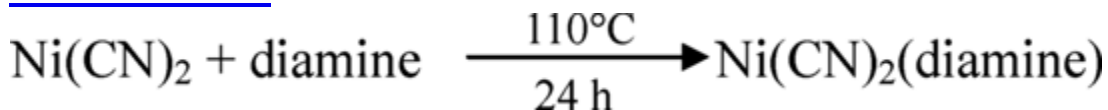
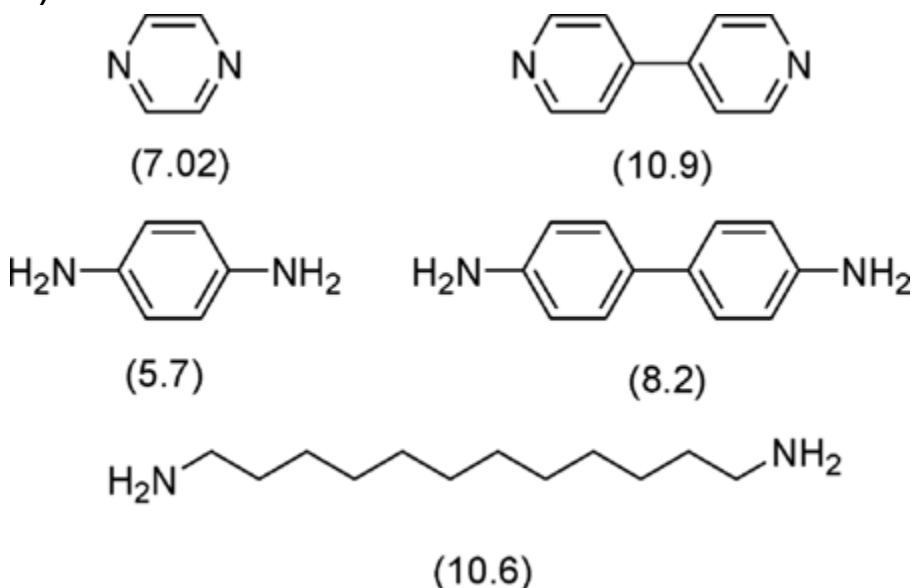


Figure 1.4 Diamines and *c*-axis values (in parentheses, Å).



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: $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$, $n = 4-8$) 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.

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.

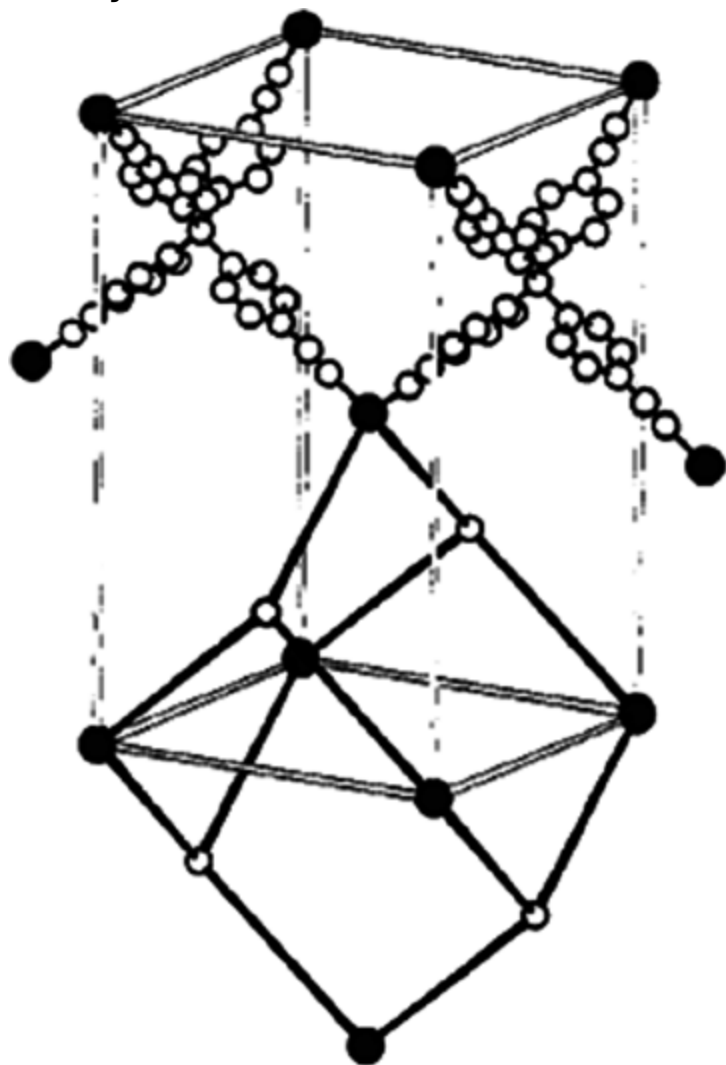
1.3.1 Organic Coordination Network: The First Example

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 $\{\text{Cu}^{\text{I}}[\text{C}(\text{C}_6\text{H}_4\cdot\text{CN}_4)]\}^+$ of tetrahedral centers linked together by rod-like units. The rod-like units were obtained by substitution of the acetonitrile ligands in $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4]^+$ 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 \AA^3 . It was estimated 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.

Figure 1.5 Tetragonal unit cell with parts of adjacent unit cells of $\{\text{Cu}^{\text{I}}[\text{C}(\text{C}_6\text{H}_4\cdot\text{CN}_4)]\}^+$. Gray circles denote the Cu atoms. The adamantane-like cavity is highlighted (black sticks). Nitrobenzene molecules and BF_4^- are omitted for clarity.

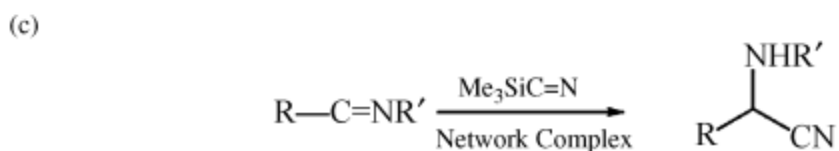
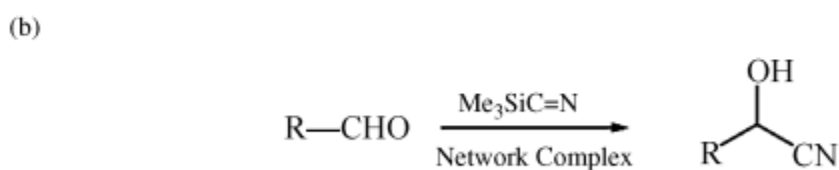
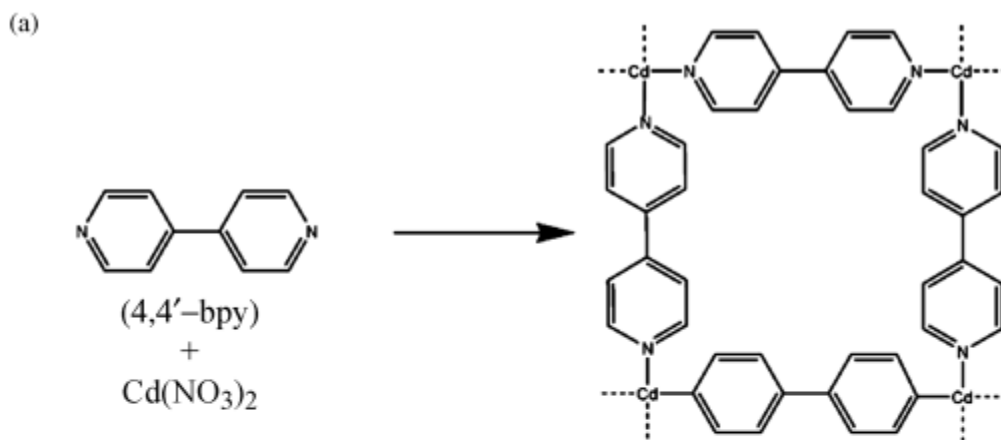


With this work Robson and coworkers established a new strategy capable of designing new solids containing large cavities by linking organic molecules with determined size and shape.

1.4 M-Bipyridine Square Grids: Two-Way Link. Toward New Functions and Applications of Organic Coordination Networks

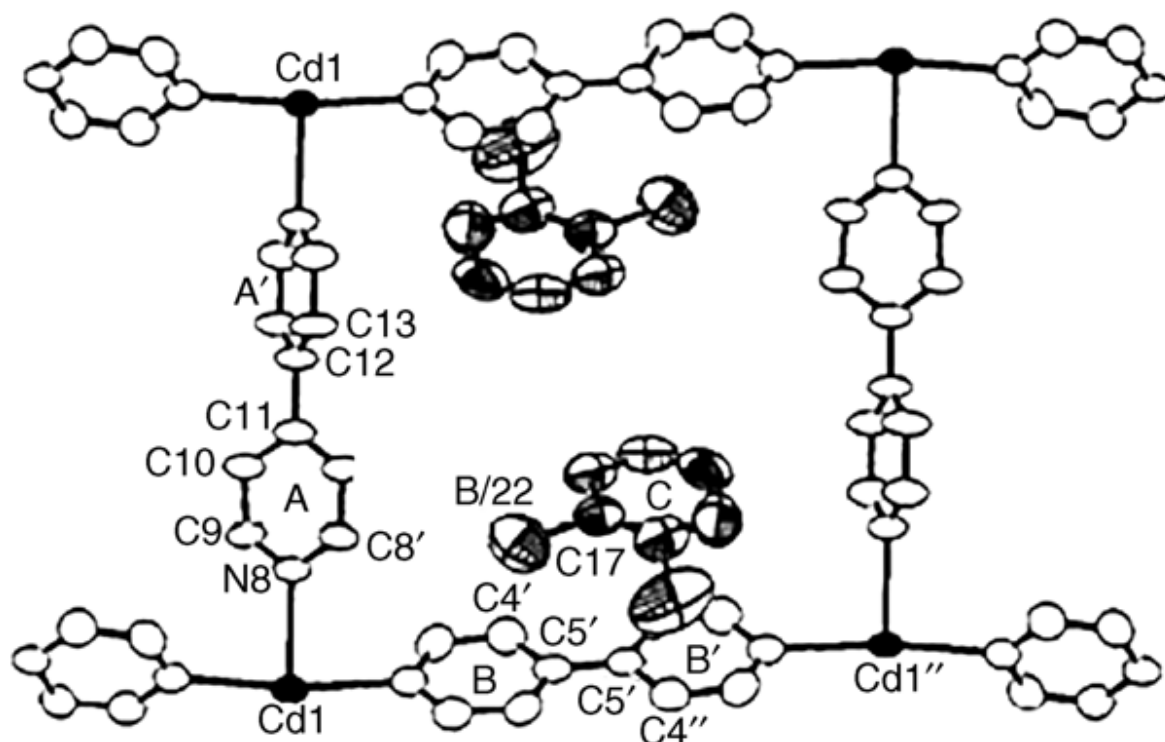
The preparation of a macrocyclic polynuclear complex $[(en)Pd(4,4'-bpy)]_4(NO_3)_8$ (bpy = bipyridine) with the ability to recognize organic molecules in aqueous environment was an important step toward the applicability of such organic coordination networks. [15] Such applicability was demonstrated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

[Scheme 1.6](#)



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](#)).

Figure 1.6 View of the complex [Cd(bpy)₂](NO₃)₂(C₆H₄Br₂)₂ showing 50% probability ellipsoids. Nitrate ions have been omitted for clarity.



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 $[\text{Zn}(4,4'\text{-bpy})_2]\text{SiF}_6$ with large non-interpenetrated channels ([Figure 1.7](#)). The effective pore size ($8 \times 8 \text{ \AA}^2$) is comparable to the pore sizes of 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.

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.* $11.396 \times 11.396 \text{ \AA}^2$.