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Porosity in Metal–Organic Compounds

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9.1 Introduction

Inorganic zeolites [1], mesoporous silica [2], and porous carbon [3] are useful materials because of their permanent porosity imparted by their architectural stability in the absence of guest molecules. The chemical functionalization and structure control of these classes of porous materials have been long-standing challenges. Indeed, the incorporation of organic functionality and transition metal ions within the structures of these porous materials remain objectives highly sought after. Inorganic and organic molecules when linked into extended structures provide vast opportunities for making porous metal–organic crystals by design and for translating molecular organic and inorganic functionality and reactivity into the solid state. Metal–organic compounds having crystal structures with open space have been known since Werner’s work on coordination complexes [4, 5]. Since that time many different classes of porous molecular crystals and extended solids have been studied, but none of these had been shown to have permanent porosity until metal–organic frameworks (MOFs) were reported in the 1990s [6–11]. This contribution highlights the structures and porous properties of important crystalline molecular complexes and extended structures dating from Werner compounds up to and including MOFs.

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9.2 Werner complexes

At the end of the 19th century, little was known about what has since been termed coordination compounds, and conclusions were mainly based on phenomenological observations. Assigned empirical formulas were entirely speculative. However, coordination compounds were in widespread practical use, such as in pigments (e.g. Prussian blue) and dyes (e.g. alizarin) [12]. No theory existed to rationalize the behavior of these materials, when Alfred Werner started his research in 1890 [13]. In the following decades he conceptualized coordination chemistry, work which was finally recognized with the award of the 1913 Nobel Prize in Chemistry. Before Werner's groundbreaking work, the formulation of metal complexes strongly relied on findings from valence theory in organic and inorganic compounds [14]. Kekulé suggested that each element could only exist in one valence and formulas were made accordingly, leading to the dot notation, e.g. $\text{CoCl}_3 \cdot 6\text{NH}_3$. This meant that cobalt shows a valence of +3 and contains six equivalents of ammonia, which described the composition of matter correctly, but provided no information concerning the actual structure. In contrast, Werner's concept postulated that there is a fixed coordination number for a given metal center, with a defined arrangement of the ligands around it. He also made a distinction between charged, e.g. Cl^- and neutral ligands, e.g. NH_3 . The Werner complex could then be formulated as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ which clearly indicates six ammonia ligands surrounding the Co^{3+} central ion [15]. In order to elucidate the binding mode at the metal center, Werner performed experiments with complexes of formula $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$ which could principally show three distinct geometries: hexagonal planar, trigonal prismatic or octahedral. Hexagonal planar and trigonal prismatic geometries would produce three isomers, whereas the octahedral geometry could only produce two isomers (Figure 9.1).

Werner confirmed the latter by isolation of only two geometrical isomers and subsequently validated that model by introduction of chelating amine ligands such as ethylenediamine. We should emphasize here that, in contrast to today's technical capabilities, Werner and his coworkers had to rely on experimental techniques, e.g. crystallization and solubility tests as well as the use of very basic characterization tools such as polarimetry and conductivity [4]. This work enabled the synthesis and characterization of an important class of Werner complexes, β - $[\text{M}(\text{PIC})_4(\text{NCS})_2]$ ($\text{M}=\text{Ni}^{2+}$, Co^{2+} , $\text{NCS} =$ thiocyanate) [16] whose crystal structure showed open spaces between the complexes (Figure 9.2) [17]. The work of Barrer in 1969 first showed that these complexes could take up gases, such as nitrogen, oxygen, noble gases, and hydrocarbons in a reversible manner [18]. Heats of adsorption were calculated and the authors finally concluded a zeolite-like sorption behavior of these molecular materials. However, these compounds lost porosity upon cycling due to their molecular structures collapsing into non-porous solids.

9.3 Hofmann clathrates

Hofmann clathrates represent an important class of materials, since they can be considered as the first coordination networks. In this context a network of formula $[\text{Ni}(\text{CN})_2(\text{NH}_3)] \cdot \text{C}_6\text{H}_6$ was prepared by Hofmann as early as 1897; unfortunately, structural characterization was not possible at that time [19]. The structure of the network therefore remained unclear for almost 60 years, until Powell and coworkers performed a successful X-ray analysis in 1952 [20]. It was discovered to be principally composed of two-dimensional layers of alternating octahedral and square planar Ni^{2+} , linearly connected through 4 CN^- moieties. The terminal NH_3 ligand is axially bound and points towards the adjacent layer, thus forming a cavity that can encapsulate benzene molecules (Figure 9.3).

Later, in the 1960s, Iwamoto and coworkers focused on a more systematic concept in synthesizing Hofmann complexes and utilized two charged components to build these networks, in addition to having neutral, encapsulated guest molecules [21, 22]. Their clathrates with general formula $[\text{M}^{\text{I}}(\text{NH}_3)_2\text{M}^{\text{II}}(\text{CN})_4] \cdot \text{G}$ ($\text{G} = \text{Guest}$)

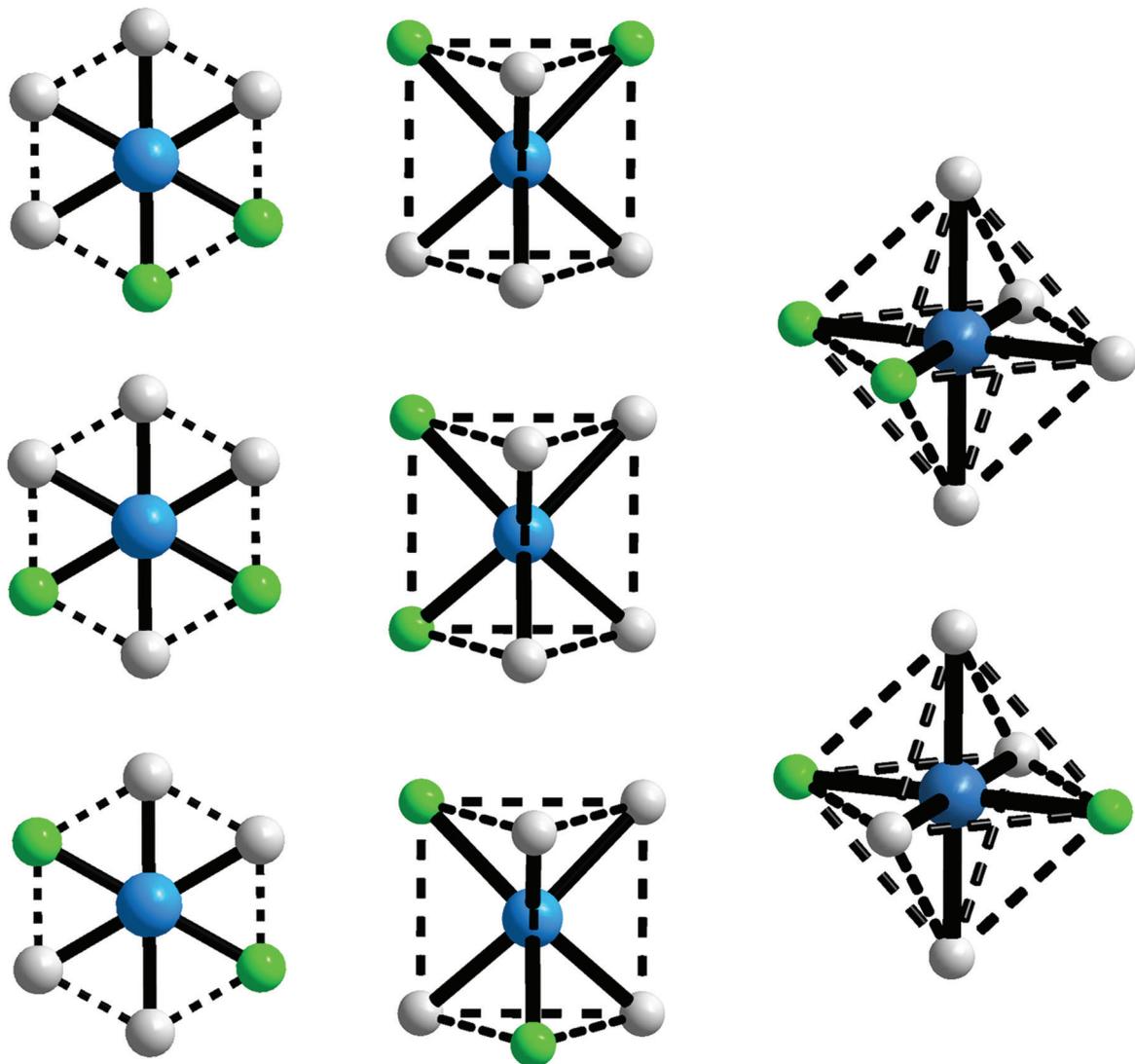


Figure 9.1 Possible geometries of the $M(\text{NH}_3)_4\text{Cl}_2$ complex. Three isomers of hexagonal planar, three isomers of trigonal prismatic and two isomers of octahedral geometry are theoretically feasible (from left to right). Color code: blue, M ; green, Cl ; light grey, NH_3

were obtained from cationic $[\text{M}^1(\text{NH}_3)_2]^{2+}$ complexes together with anionic square planar $[\text{M}^2(\text{CN})_4]^{2-}$ complexes and two molecules of benzene, aniline, pyrrole or thiophene. The structural characterization was performed by refinement from X-ray powder diffraction data. In 1967, Walker and Hawthorne replaced the ammonia ligand by an n -alkylamine and synthesized nickel cyanide complexes [23]. The next logical step forward was again reported by Iwamoto et al., who first introduced ethylenediamine into these types of networks [24]. The use of this bifunctional linker enabled the formation of an organic bridge between the square $\text{M}(\text{CN})_2$ layers. Encapsulation of aromatic guests such as aniline, benzene, thiophene, or pyrrole was

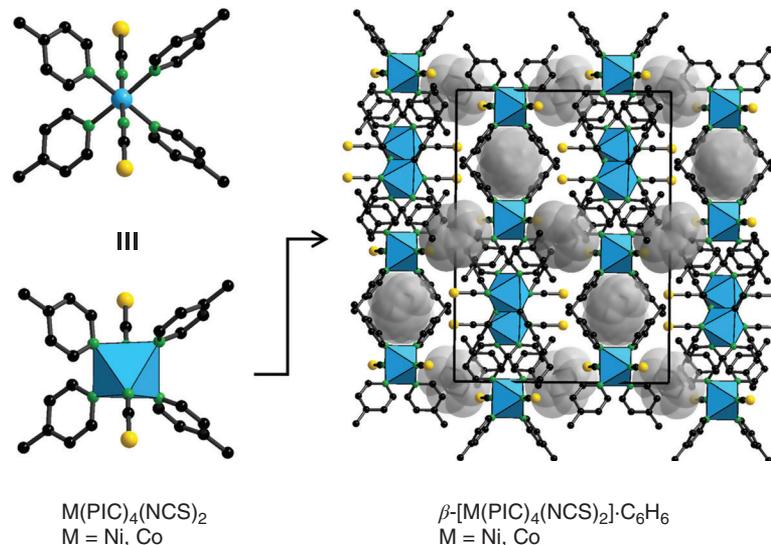


Figure 9.2 Werner complexes of formula $\beta\text{-}[M(\text{PIC})_4(\text{NCS})_2]$ ($M = \text{Ni}^{2+}, \text{Co}^{2+}$, PIC = γ -picoline) (left). The crystal packing, depicted along the [010] axis, shows the encapsulation of benzene molecules (shown in space-filling representation) occupying the zigzag channels between the complexes. Color code: black, C; green, N; yellow, S; blue polyhedra, M

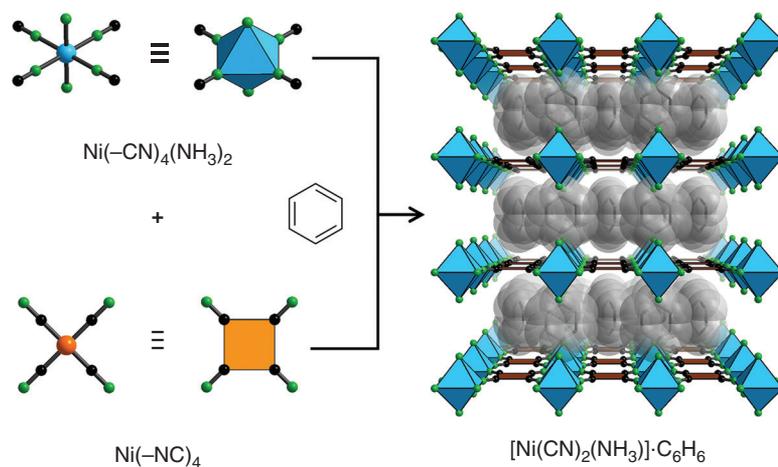


Figure 9.3 Single-crystal X-ray structure of the original Hofmann clathrate $[\text{Ni}(\text{CN})_2(\text{NH}_3)]\cdot\text{C}_6\text{H}_6$ as analyzed by Powell and coworkers [20]. The structure is reproduced from given atomic coordinates; benzene guest molecules are shown in the space-filling model between the two-dimensional $[\text{Ni}(\text{CN})_2(\text{NH}_3)]$ layers. Hydrogen atoms are omitted for clarity. Color code: black, C; green, N; blue and orange polyhedra, Ni

successfully demonstrated. Mathey and coworkers then further expanded this concept in 1977 to show that variation of linker length provides the opportunity for selective rather than random encapsulation of aromatic guests and solvents [25, 26]. Later, Iwamoto et al. followed up and synthesized a series of α,ω -diaminoalkane complexes; each deliberately designed to encapsulate specific molecules (Figure 9.4) [27, 28].

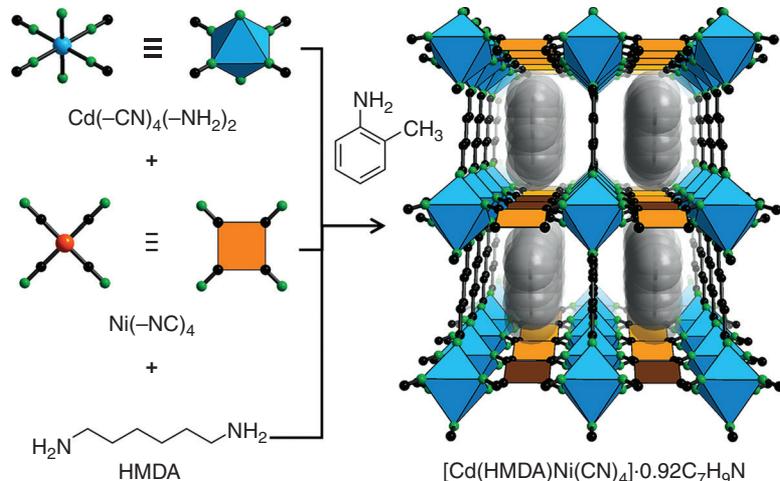


Figure 9.4 Single-crystal X-ray structure of the Hofmann clathrate $[\text{Cd}(\text{HMDA})\text{Ni}(\text{CN})_4] \cdot 0.92\text{C}_7\text{H}_9\text{N}$ (HMDA = hexamethylene-1,6-diamine) sustained by α,ω -diaminoalkanes. The encapsulated *o*-toluidine (shown in space-filling model) appears disordered. Hydrogen atoms are omitted for clarity. Color code: black, C; green, N; orange polyhedra, Ni; blue polyhedra, Cd

All these valuable contributions established early principles of materials design, and clearly showed how linker length can control material properties, enabling selectivity at the molecular level. The concept introduced at that time provided the foundation for the synthesis of modular coordination polymers, a term first used by John Bailar in 1963 to describe Beryllium-bis-(β -diketone) complexes [29]. Although these are not polymers but extended crystals, the term is still in use today. We note that although Hofmann clathrates and related compounds showed absorption of guests from liquid phase, no examination by gas adsorption at low-temperature (the golden standard of measuring permanent porosity) was performed until 1995 when Ramprasad et al. demonstrated that lithium pentacyanocobaltate coordination networks of formula $\text{Li}_3[\text{Co}(\text{CN})_6] \cdot 4\text{DMF}$ (DMF = *N,N*-dimethylformamide) show reversible oxygen sorption at room temperature [30]. The type I isotherm, fitted to the Langmuir model, was explained by a reversible chemisorption of O_2 ; however, the material did not exhibit pores. It was rather suggested that the oxygen uptake was occurring via a solid state diffusion mechanism. A point to make about the cyano-based frameworks is that the cyanide ion is not functionalizable and that the pillaring organic units may serve as functionalization points to some limited degree.

9.4 Coordination polymers

Coordination polymers, even if the term had not been used at that time, can be dated back to 1959, when Saito et al. crystallized the first bis(alkylnitrilo)copper(I) structures in an attempt to gain insights to the dyeing of polyacrylonitrile fibers [31–33]. The obtained structures were characterized by means of single-crystal X-ray diffraction. They are composed of tetrahedral $\text{Cu}(-\text{CN})_4$ units that have been known to coordination chemists since the early 20th century [34]. These building units are connected through organic moieties with different length and thus propagate into extended networks of varying dimensions. Depending on the length and conformation of the dinitrile linker, one-dimensional chains, in the case of succinonitrile (SUC), two-dimensional grid structures, in the case of glutaronitrile (GLU) or three-dimensional networks, in the case of adiponitrile (ADI) were obtained (Figure 9.5).

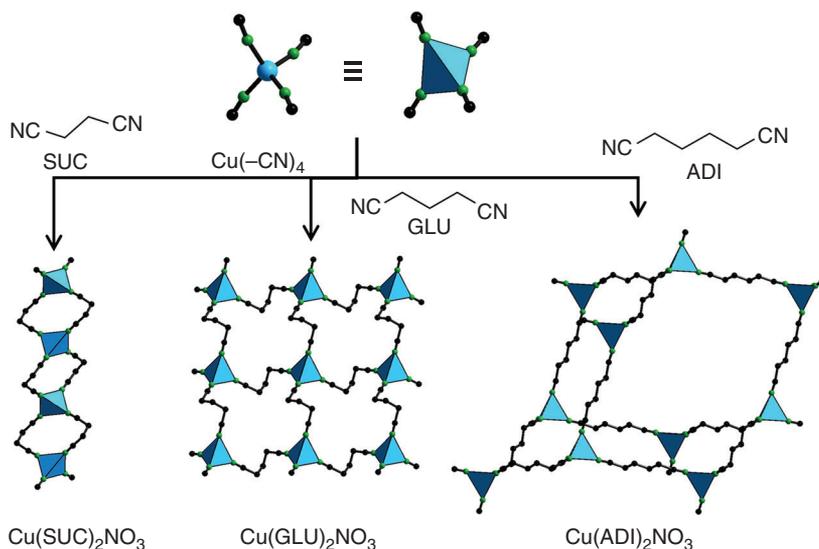


Figure 9.5 Diverse bis(alkylnitrilo)copper(I) structures: one-dimensional chains sustained by succinonitrile (SUC) [31], two-dimensional grid structures with glutaronitrile (GLU) linkers [32], and three-dimensional networks made of adiponitrile (ADI) linkers [33]. Hydrogen atoms, anions, and interpenetrating networks are omitted for clarity. Color code: black, C; green, N; blue polyhedra, Cu

In this context, bis(adiponitrilo)copper(I) nitrate deserves special attention since it represents the first three-dimensional, four-connected network reported. The authors classified it correctly as a diamond lattice according to the geometry principles of crystal chemistry established by A. F. Wells in 1954 [35]. The relative length of the organic linker and the resulting large open architecture led to the formation of six interpenetrated nets [36] to fill the void space of the adamantine cage.

Besides several other one- or two-dimensional nets, a diamond-like coordination polymer was synthesized in 1986 by Hünig and co-workers in an attempt to synthesize a radical anion salt of 2,5-dimethyl-*N,N'*-dicyanoquinonediimine with high electrical conductivity [37]. However, the structural outcome was not discussed in detail, though it shows a seven-fold interpenetrated diamond net. This particular compound was later derivatized by Kobayashi et al., using methoxy-, chloro- and bromo-substituted linkers with retention of the overall structure [38].

In 1989, Hoskins and Robson provided an important rationale for the deliberate design and synthesis of extended nets. In their contribution they utilized the tetrahedral single-metal building unit $\text{Cu}(-\text{CN})_4$ together with the tetrahedral organic linker 4,4',4'',4'''-tetracyanotetraphenylmethane (TCTPM) to afford an infinite, non-interpenetrated, cationic framework of formula $[\text{Cu}(\text{TCTPM})]^+$ (Figure 9.6) [39]. This framework contains charge balancing BF_4^- counteranions as well as neutral nitrobenzene guests in an adamantine cavity that was estimated to be around 700 \AA^3 in volume. It was further proved that the BF_4^- anions are indeed exchangeable through PF_6^- without disturbing the framework's integrity.

Many diamond-like frameworks have subsequently evolved based on the simple design principles from tetrahedral building units. The shortest moieties in this context were CN^- , to yield isostructural, two-fold interpenetrated $\text{M}(\text{CN})_2$ nets, where $\text{M} = \text{Zn}, \text{Cd}$ [40, 41]. The introduction of longer linkers, such as 1,4-dicyanobenzene, 4,4'-dipyridyl or 2,5-dimethylpyrazine together with Cu^I afforded five-fold, four-fold and one-fold interpenetrated diamond networks. In all these cases, the anions (BF_4^- or PF_6^-) reside in the channels and do not interact with the metal cations [42].

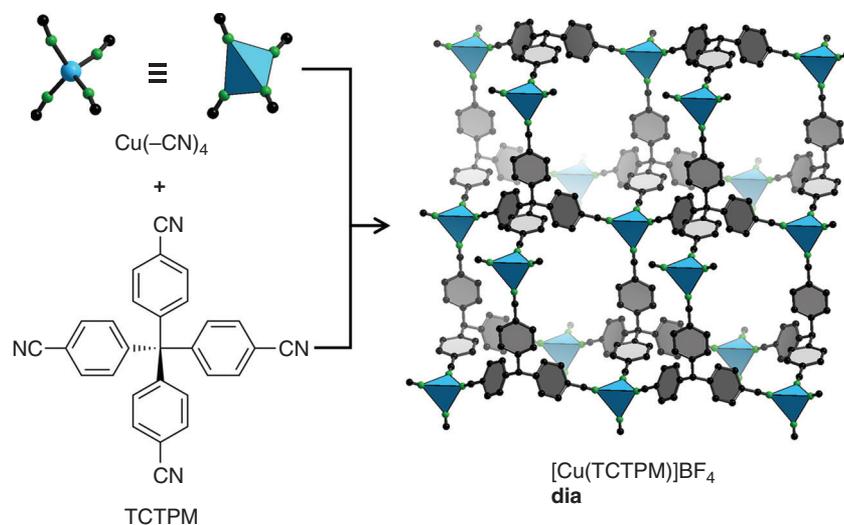


Figure 9.6 Diamond-like framework composed of tetrahedral single-metal building units $\text{Cu}(-\text{CN})_4$ and tetrahedral organic linkers. Anions and solvent molecules were found heavily disordered and were not refined. Hydrogen atoms are omitted for clarity. Color code: black, C; green, N; light blue polyhedra, Cu

Although diamond-type frameworks were predominant at that time, other nets structurally related to platinum(II) sulfide (**pts**) were synthesized by replacing the tetrahedral (S^{2-}) and the square planar (Pt^{2+}) through Cu^+ and $[\text{Pt}(\text{CN})_4]^{2-}$ respectively [43]. This strategy resulted in an anionic open framework structure, containing hexagonal channels partially filled with charge balancing $[\text{NMe}_4]^+$ cations. The contribution provided further evidence that geometric design principles were feasible for the synthesis of frameworks; however, a general concept had to be developed.

Following this initial strategy, in 1994, a tetracyano-functionalized porphyrin (TCP) linker was introduced as a square planar building unit of the PtS-type framework $\text{Cu}^{\text{II}}(\text{TCP})\text{Cu}^{\text{I}}\text{BF}_4$ (Figure 9.7, left) [44]. This net shows two-fold interpenetration which could be avoided through structure fine-tuning based on pyridine-derived linkers. We note here that Cu^{II} resides in the center of the porphyrin linker, whereas Cu^{I} serves as a tetrahedral single-metal building unit. The tetrapyrrolyl-functionalized porphyrin (TPP) network $\text{Cu}^{\text{II}}(\text{TPP})\text{Cu}^{\text{I}}\text{BF}_4$ (Figure 9.7, right) relies on a single net without interpenetration, which the authors attribute to the steric bulk of the pyridyl- in comparison to the cyano-functionality.

Later, in 1995, this building block approach was utilized to combine tritopic cyano-based linkers with Ag^{I} cations to afford networks that exhibit either AlB_2 (**alb**) or ThSi_2 (**ths**) topology [45]. The latter contains channels of inner diameter 15 \AA and thus enables guest exchange by retaining framework crystallinity.

In summary, cyano-based structures have long been well known to coordination and supramolecular chemists. The initial results, which appeared rather serendipitous throughout the 1960s to 1980s, were conceptualized in the 1990s according to simple geometric design principles. The use of the molecular building block approach [46] rendered these coordination polymers into fine-tunable materials, though with strong limitations at that time. Nonetheless, the results paved the way for the design of materials with superior properties and levels of synthetic control hitherto unknown to materials chemists.

Although there had already been many reports on pyridine based structures, it took until 1994 for the first two-dimensional square grid network with catalytic activity to be reported [47]. It is composed of $\text{Cd}(\text{BIPY})_2(\text{NO}_3)_2$ (BIPY = 4,4'-bipyridine) and contains large guest-filled voids that can render catalytic processes with respect to cyanosilylation. The framework was derived from a closely related molecular material

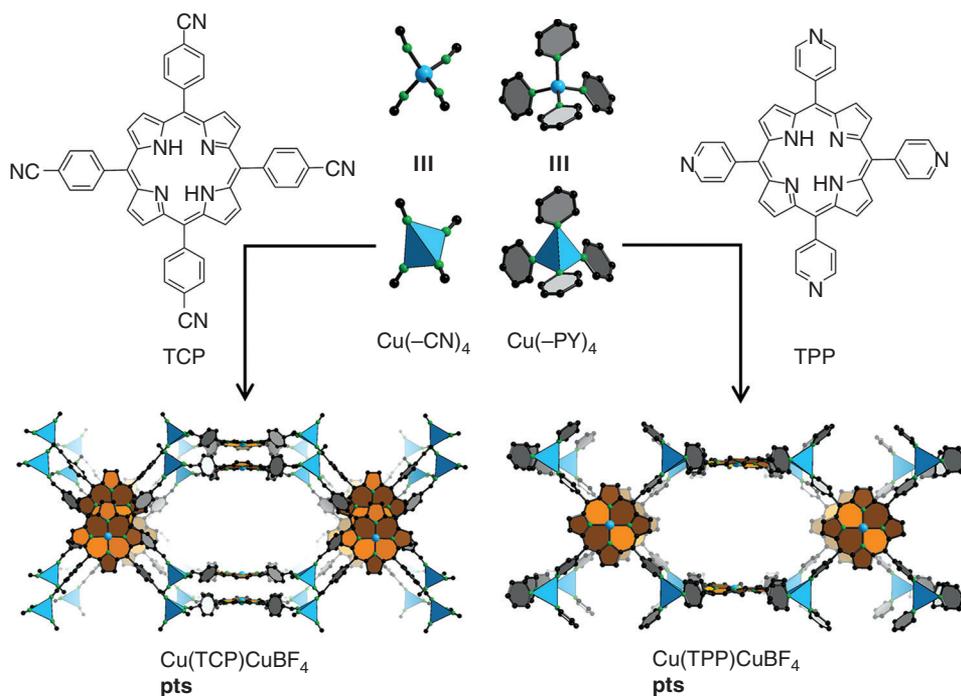


Figure 9.7 Comparison of the two-fold interpenetrated framework $\text{Cu}^{\text{II}}(\text{TCP})\text{CuBF}_4$ and the single net $\text{Cu}^{\text{II}}(\text{TPP})\text{CuBF}_4$. Hydrogen atoms, solvent molecules and anions are omitted for clarity. Color code: black, C; green, N; light blue, Cu^{II} ; light blue polyhedra, Cu^{I}

where square planar Pd^{II} ions are capped in a *cis*-fashion by ethylenediamine [48]. The two remaining coordination sites then connect through BIPY to yield a molecular square. Based on this structure, the extended two-dimensional $\text{Cd}(\text{BIPY})_2(\text{NO}_3)_2$ was synthesized. Single-crystal X-ray diffraction provided evidence that the structure forms a clathrate with *o*-dibromobenzene that sits inside the square microchannels of the framework (Figure 9.8).

More importantly, the first catalytic process within a coordination polymer was addressed through cyanosilylation of benzaldehyde and imines. Although compounds of formula $[\text{M}(\text{BIPY})_2(\text{H}_2\text{O})]\text{X}$ ($\text{M} = \text{Zn}^{2+}$, Cd^{2+} , Cu^{2+} ; $\text{X} = \text{PF}_6^-$, SiF_6^{2-}) and $[\text{Cd}(\text{BIPY})_2(\text{H}_2\text{O})_2]\text{PF}_6 \cdot 2(\text{BIPY}) \cdot 4\text{H}_2\text{O}$ have previously been reported, they were not investigated for guest encapsulation or catalytic performance [49, 50]. In such cases interpenetration has precluded the formation of cavities and thus hampered clathrate formation or catalysis. We therefore believe, that $\text{Cd}(\text{BIPY})_2(\text{NO}_3)_2$ can be considered special since it inspired researchers to explore these particular types of networks, which has led to numerous elegant examples of $\text{M}(\text{BIPY})_2$ square grids [51–55]. Some of them show interesting properties, especially in terms of gas storage and separation and still represent a very active branch of MOF research up to date. We consider certain contributions on $\text{M}(\text{BIPY})_2$ and related materials that emerged through the mid-1990s as essential for the development of MOFs, and will discuss them here.

The term metal–organic frameworks, abbreviated to MOFs, was first coined in 1995 initially referring to a compound with formula $\text{Cu}(\text{BIPY})_{1.5}(\text{NO}_3)$ that shows a diamond-like structure composed of Cu^{I} and 4,4'-bipyridine (Figure 9.9) [56]. Since then, thousands of MOFs, sometimes also termed porous coordination polymers (PCPs), have appeared in the open literature [9].

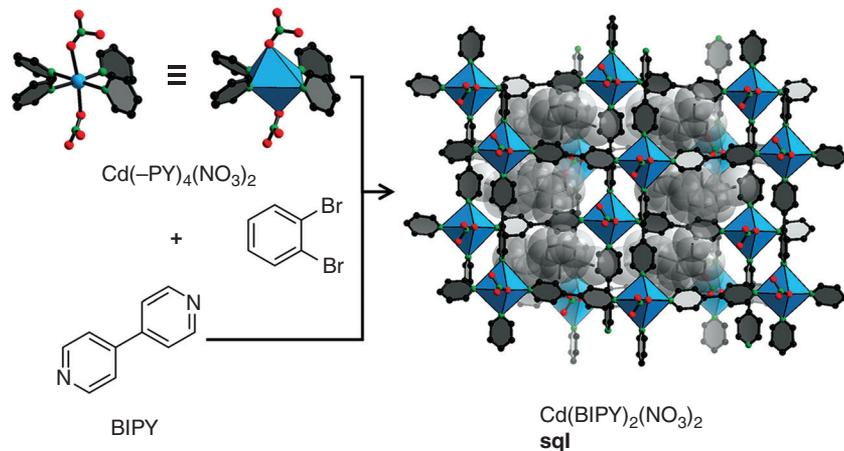


Figure 9.8 Square grid net of formula $\text{Cd}(\text{BIPY})_2(\text{NO}_3)_2$ shown approximately along the crystallographic [001] axis. It forms a clathrate with *o*-dibromobenzene molecules (depicted in space-filling representation) that reside inside the square microchannels. Hydrogen atoms are omitted for clarity. Color code: black, C; red, O; green, N; blue polyhedra, Cd

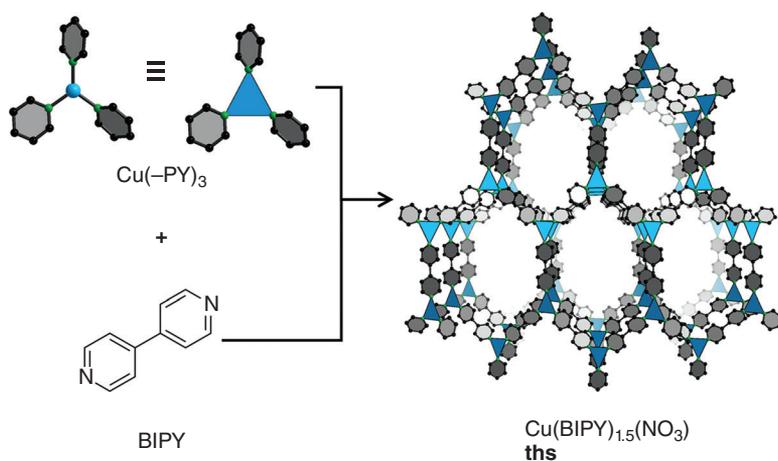


Figure 9.9 Left: triangular Cu^I building units connected through 4,4'-bipyridine; right: the overall cationic three-dimensional ThSi_2 (**ths**) topology framework is based on linearly connected triangular units. Hydrogen atoms, solvent molecules, charge balancing anions, and interpenetrating networks are omitted for clarity. Color code: black, C; green, N; blue polyhedra, Cu

$\text{Cu}(\text{BIPY})_{1.5}(\text{NO}_3)_2$ is composed of a triangular $\text{Cu}(-\text{PY})_3$ building unit connected by 4,4'-bipyridine into an extended framework with ThSi_2 (**ths**) topology. The six interpenetrated nets contain charge-balancing anions that reside in the rectangular channels with dimensions of 3×6 and $6 \times 6 \text{ \AA}$. The nitrate ions were demonstrated to be exchangeable with other simple inorganic anions such as BF_4^- or SO_4^{2-} . The contribution also demonstrated that hydrothermal synthetic conditions represent a viable route to such frameworks, resembling a route that has proved fruitful in zeolite chemistry.

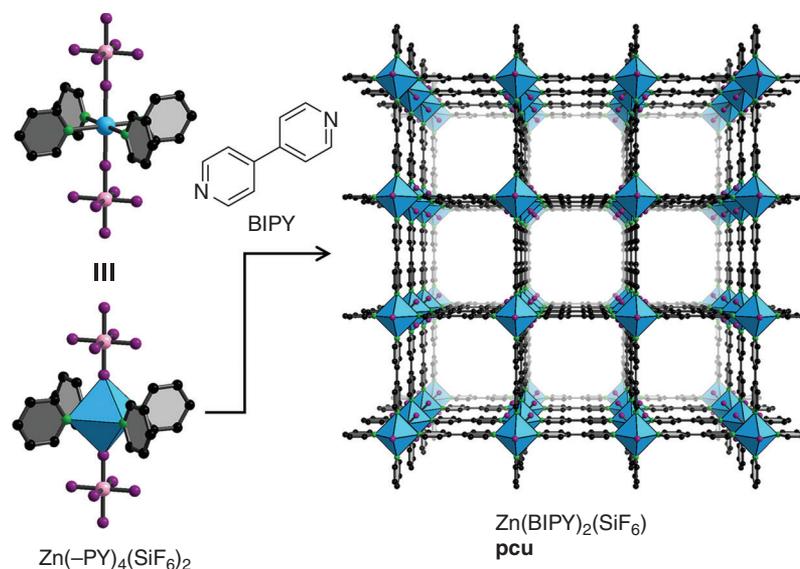


Figure 9.10 Single-crystal X-ray structure of $\text{Zn}(\text{BIPY})_2(\text{SiF}_6)_2$; the two-dimensional net is connected through SiF_6^{2-} anions to give a 3D framework with rectangular channels of $8 \times 8 \text{ \AA}$ along the crystallographic [001] direction. Color code: black, C; green, N; purple, F; rose, Si; blue polyhedra, Zn

In the same year, another three-dimensional net was reported, based on octahedral $\text{Zn}(-\text{PY})_4(-\text{SiF}_6)_2$ building units [57]. The resulting framework consists of an octahedral Zn^{2+} cation coordinated to four BIPY linkers into a square grid net that is in turn axially pillared by anionic SiF_6^{2-} moieties. Preparation of $\text{Zn}(\text{BIPY})_2(\text{SiF}_6)_2$ under certain synthetic conditions then led to the formation of a non-interpenetrated open framework with a primitive cubic (**pcu**) topology showing large square channels along the crystallographic [001] axis (Figure 9.10).

These channels have dimensions of $8 \times 8 \text{ \AA}$, and the empty space generated comprises about 50% of the total unit cell volume. We note here that the Zn-version of this material was reported to be unstable upon loss of guest molecules under vacuum, and that the Cu-analogue shows a surface area of $1337 \text{ m}^2\text{g}^{-1}$ [54]. This material was reported in 2000 and is, today, one of the best sorbents for methane in terms of volumetric uptake at room temperature.

After these seminal contributions it took more than ten years for it to be discovered that materials of composition $\text{Cu}(\text{BIPY}-n)_2(\text{SiF}_6)_2$ (BIPY-*n* generally represents 4,4'-bipyridine or its derivatives, i.e. linear linkers with two terminal aromatic nitrogen donor moieties) are exceptional with respect to CO_2 uptake and separation [58, 59]. These materials were shown as amenable to structure fine-tuning and to be stable under humid conditions, which makes them one of the best-performing materials for this particular application to date.

9.5 Porosity in metal–organic frameworks

Previous experiments on reversible sorption of small molecules in Werner complexes, such as $\beta\text{-M}(\text{PIC})_4(\text{NCS})_2$ ($\text{M} = \text{Ni}^{2+}, \text{Co}^{2+}$), Prussian Blue of general formula $\text{Fe}_4[\text{Fe}(\text{CN})_6]$ and Hofmann clathrates have already been established and well-documented. Many crystal structures of coordination polymers following the structure classification of “node” and “linker” put forward by Wells have been reported all

throughout the last 70 years or so. One of us (O.Y.) recalls in the early 1990s chemists commenting about these structures that they were “sculptures rather than useful materials.” This underlined the need for developing strategies for making robust frameworks that exhibit permanent porosity so that they can be utilized in many applications such as separations and catalysis. A strategy reported in 1998 outlined the use of carboxyl functionality to lock the metal–ion positions in place and allow for robust metal–carboxyl clusters to be used as nodes in making extended structures. The other advantage of these clusters was that they had one kind of an overall coordination mode and therefore there was no ambiguity as to the coordination geometry to be adopted upon formation of the network; a factor coordination polymers suffered from, and one that prevented the making of structures by design.

Thus in 1998, MOFs gained traction due to the first report establishing microporosity by surface area and pore volume determination. In particular, a material, named MOF-2, with formula $Zn_2(BDC)(H_2O)$ (BDC=1,4-benzenedicarboxylate) was synthesized and shown to contain potential voids filled with DMF and H_2O guest molecules, respectively (Figure 9.11) [60]. The structure is composed of $Zn_2(-COO)_4(H_2O)_2$ paddlewheel-like secondary building units (SBUs) that are in turn connected by BDC linkers. The resulting two-dimensional grid network is held together by strong hydrogen-bonding interactions among the axial water molecules as well as the carboxylate moieties on the paddlewheel units.

The guests can be removed under vacuum with heating to yield the desolvated structure $Zn(BDC)$. Gas adsorption studies demonstrated that this material is permanently microporous, as exemplified by reversible type I gas sorption isotherms using nitrogen at 77 K (Figure 9.12) or carbon dioxide at 195 K as sorbates. These experiments enabled the estimation of Langmuir apparent surface areas between 270 and 310 $m^2 g^{-1}$, as well as micropore volumes between 0.094 and 0.086 $cm^3 g^{-1}$.

Other materials that validated the existence of permanent porosity in MOFs are represented by structures later termed as MOF-3 and MOF-4, $Zn_3(BDC)_3$ and $Zn_2(BTC)(NO_3)$ (BTC=1,3,5-benzenetricarboxylate) respectively [7, 61, 62], MOF-3 was initially reported in 1998 and is composed of a trimeric zinc SBU that is in turn coordinated to six carboxylate groups of BDC [61]. This affords an overall three-dimensional framework with rhombic shaped pores, filled with methanol guest molecules. In addition, the remaining four coordination sites at the SBU were occupied by methanol, giving rise to potential open metal sites (OMS). The apparent surface area of this material was estimated in a later contribution to be 140 $m^2 g^{-1}$. MOF-4 was first reported in 1997 by reacting zinc nitrate together with H_3BTC at room temperature. The resulting framework

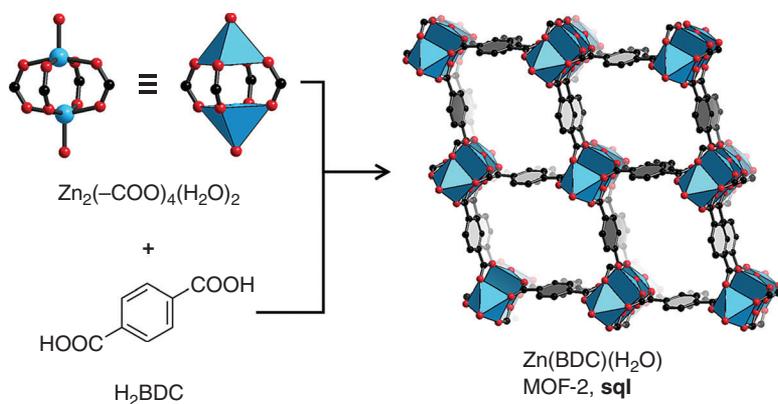


Figure 9.11 View of MOF-2 along the crystallographic [001] direction, the rectangular channels are clearly visible. Hydrogen atoms, except on terminal water ligands, and solvent molecules, are omitted for clarity. Color code: black, C; red, O; blue polyhedra, Zn

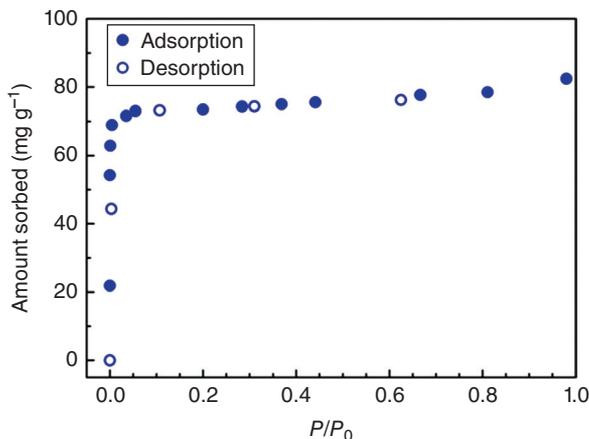


Figure 9.12 Gas adsorption isotherm for MOF-2 with N_2 at 77 K. This served as the first example of microporosity reported in a metal–organic framework

is composed of a trimeric $Zn_2(-COO)_3(NO_3)$ SBU that is connected to two other SBUs through a BTC linker to afford a three-dimensional framework [62]. Remaining coordination sites are occupied by ethanol solvent molecules. It was later proven by ethanol-sorption experiments, that MOF-4 is also a permanently porous structure.

These seminal contributions, especially the discovery of microporosity in MOF-2, imparted momentum to the development of structures based on paddlewheel SBUs and spurred interest in exploitation of new carboxylate based clusters as building blocks for MOFs. We note here that other MOFs have previously appeared in the literature together with reported gas sorption isotherms. Herein, the T-shaped $Co_2(BIPY)_3(NO_3)_4$ readily adsorbs gases such as methane, nitrogen, and oxygen at high pressures (up to 36 atm) [63]. However, since the experiments were performed at room temperature and not at the boiling point of the particular gas, an estimation of the apparent surface area and pore volume was not possible. The gas adsorption isotherm at 77 K is the gold standard for proof of porosity.

9.6 The discovery of MOF-5: the golden age of metal–organic frameworks

MOF-5 is recognized as the most prominent example of a metal–organic framework by many researchers in material science but also from other fields of chemistry (Figure 9.13) [64].

The enormous popularity of this structure, in our view, has three main causes: the advantage of a simple network accessible through rational design principles, a facile route of preparation, and a very high porosity, in fact the highest porosity of any material at the time. We will therefore provide an overview of MOF-5 and its features as well as discussing other materials that helped to popularize the field at this early stage.

In 1999, little was known about porosity of metal–organic frameworks, since MOF-2 and its associated microporosity had just been discovered. This shifted the interest of many researchers from pyridine- toward carboxylate-based frameworks and thus represented a turning point in the field. At that time, the first MOF based on linking of octahedral basic zinc acetate building units, $Zn_4O(-COO)_6$, was reported. The resulting framework shows primitive cubic (**pcu**) topology and was termed MOF-5. The name was coined in reminiscence of the famous zeolite ZSM-5.

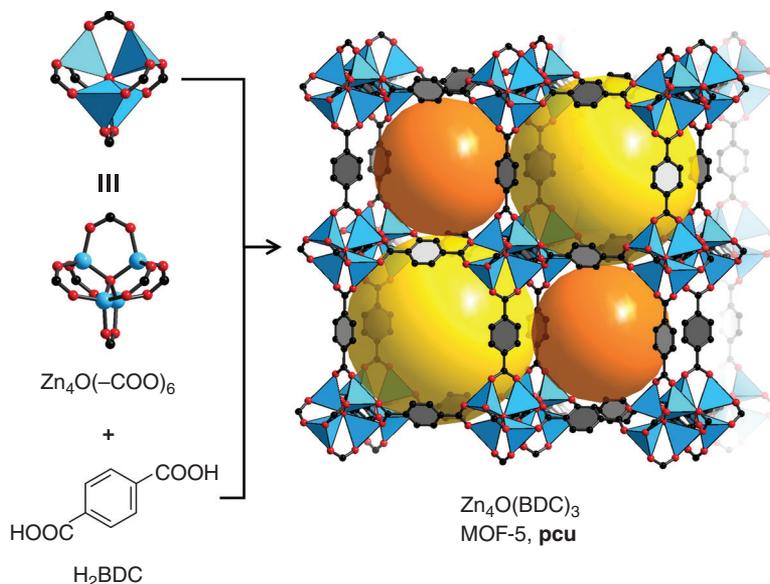


Figure 9.13 Single-crystal X-ray structure of MOF-5 constructed from $Zn_4O(-COO)_6$ SBUs, connected through BDC. The overall structure is composed of a large cavity (15.1 Å, yellow sphere) together with a smaller cavity (11.0 Å in diameter, orange sphere) in an alternating fashion. Hydrogen atoms are omitted for clarity. Color code: black, C; red, O; light blue polyhedra, Zn

The SBU of MOF-5 is composed of a tetrahedral central oxide surrounded by four tetrahedrally coordinated Zn^{2+} ions which are in turn coordinated by a total of six bridging carboxylate groups ($-COO$). This SBU represents a well-known cluster entity that has previously been obtained as discrete complexes with monocarboxylates such as acetate, benzoate, and pivalate [65].

MOF-5 was synthesized by solvothermal reaction of zinc nitrate tetrahydrate and H_2BDC in a mixture of DMF and chlorobenzene. The authors were able to show that the resulting framework contains voids filled with DMF and chlorobenzene guests, which are readily exchangeable with chloroform that could later be removed under vacuum at room temperature. The desolvated crystals kept their integrity, and nitrogen gas adsorption experiments at 77 K revealed a type I isotherm with an estimated Langmuir surface area of 2,900 m^2g^{-1} and a pore volume of 1.04 cm^3g^{-1} (Figure 9.14). These values exceeded by far all known conventional porous materials such as zeolites, silicates, or porous carbon.

It was later shown that MOF-5 is a modular structure and several isorecticular (based on the same net or topology, here a **pcu** net) frameworks could be obtained by variation of length and functionality of the linker [66].

At around the same time, another prototypical MOF, of formula $Cu_3(BTC)_2(H_2O)_3$, was synthesized and termed HKUST-1 (HKUST=Hong Kong University of Science and Technology) [67]. This structure is composed of a $Cu_2(-COO)_4$ paddlewheel SBU, similar to the one that sustains MOF-2. The SBU is connected to triangular BTC to form an overall 3,4-c twisted boracite (**tbo**) network (Figure 9.15). The $Cu_2(-COO)_4(H_2O)_2$ paddlewheel cluster has also been known for quite some time since it sustains the structure of molecular copper(II)-acetate hydrate and other transition metal analogues such as Mo or Rh [68, 69]. Removal of the terminal water ligands is possible and generates the anhydrous MOF $Cu_3(BTC)_2$, with a color change of the material from blue to purple. Surface area analysis was performed and yielded a Brunauer-Emmett-Teller (BET) area of around 700 m^2g^{-1} , which indicates a not fully desolvated structure. More recent BET measurements of this material have yielded around 1800 m^2g^{-1} after full activation [70]. In the following years, the modularity of the **tbo** net was

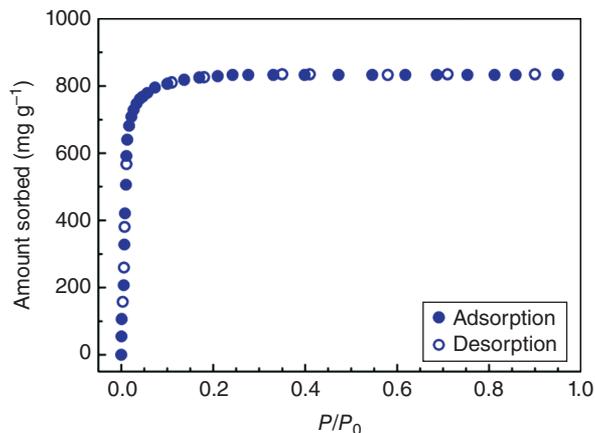


Figure 9.14 Nitrogen gas adsorption isotherm for MOF-5 at 77 K. The microporous nature of the material is indicated by a type I isotherm

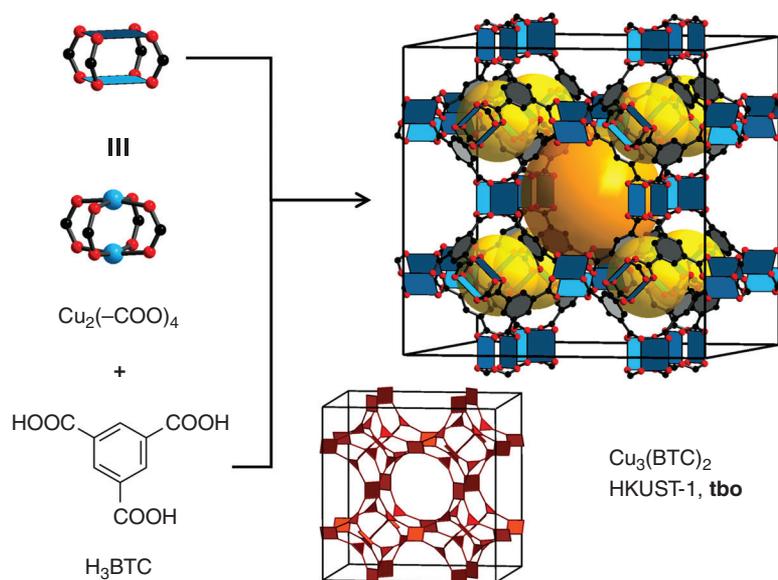


Figure 9.15 HKUST-1 synthesized by a combination of $\text{Cu}_2(-\text{COO})_4$ and BTC. Hydrogen atoms and solvent molecules are omitted for clarity. Color code: black, C; red, O; blue, Cu. The yellow and orange balls represent the empty space in the framework

further explored by the synthesis of isorecticular variants [71], with MOF-399 holding the record for the lowest density MOF (0.126 g/cm^3) known to date [72].

In summary, by end of the 1990s, MOFs started to attract considerable scientific interest due to the discovery of ways to design high surface area materials, unparalleled for conventional inorganic and organic porous materials. The materials display a large structural diversity based on different SBUs and linkers. Therefore, MOF-5 and HKUST-1 are prototypical for this class of material and are still under investigation by many research groups around the world, even 15 years after their initial discovery.

9.7 The Cambridge Structural Database – an essential tool for MOF chemists

In the context of more than 20,000 metal–organic frameworks made during the past decade, an essential resource for researchers is a database where crystal structures and related literature of existing materials can be retrieved in a facile and systematic manner. The Cambridge Structural Database (CSD), which is a part of the Cambridge Crystallographic Data Centre (CCDC), is ideally suited for this purpose since it represents a resource for small molecules containing a wide range of organic, metal–organic and organometallic crystal structures [73, 74]. We introduce discussion of this particular database here in order to give an overview of history, and, more importantly, describe the basic features of this powerful research tool.

The CCDC as a part of the Department of Chemistry at the University of Cambridge was principally established in 1965 by Dr. Olga Kennard, together with a handful of coworkers. They compiled, organized, and gradually included the relatively small number of crystal structures published at that time into a database, the CSD. Through constant development in the late 1970s and 1980s, systems for search, retrieval, analysis, and visualization of CSD information began to emerge and are still under constant improvement today. Having these systematic search capabilities, the CSD became a useful tool for what has later been termed “data mining” in fundamental research [75, 76]. The CCDC started to serve academia as well as major pharmaceutical companies during the 1980s, and it finally became an independent self-financing non-profit institution in 1989. On October 19, 2015 the CSD recorded its 800,000th structure, and is showing exponential growth, with more than 40,000 structures currently added per year, thus leading to a doubling time of around 9 years. A statistic that can be retrieved from the CSD clearly shows that the number of MOF structures increases exponentially, with today over 6000 newly reported structures per year (Figure 9.16). These enormous research efforts are mainly related to carboxylates, which have exceeded all other linker types by far (Figure 9.16 inset). This in turn means that two-thirds of all newly reported MOF structures nowadays are based on robust carboxylate linkers.

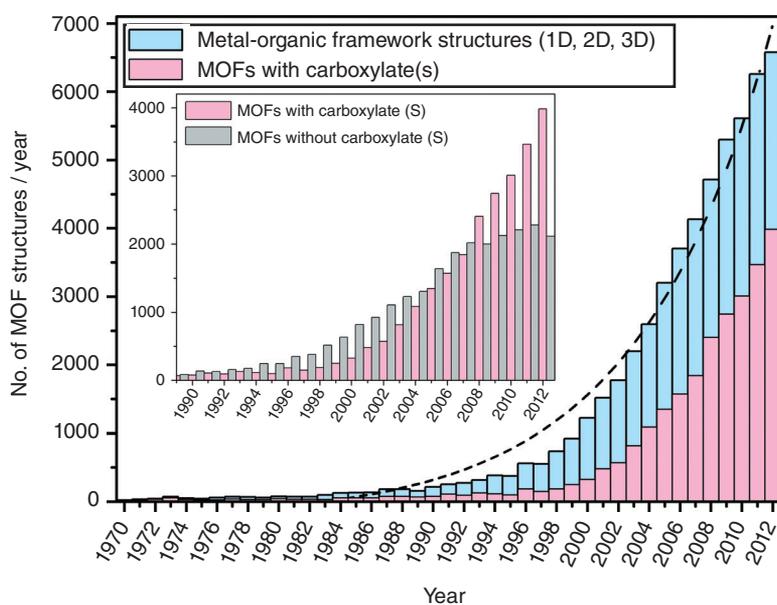


Figure 9.16 A statistic obtained from the CSD revealed an exponential increase of reported metal–organic framework structures (1D, 2D and 3D) over the decade to 2012. Notably, the utilization of carboxylate moieties represents a turning-point in the late 1990s, and now exceeds all other types of linkers by far (see inset)

New structural data are acquired by the CCDC in form of crystallographic information files (.cif), standardized text files according to the International Union of Crystallography (IUCr) [77, 78]. These are almost exclusively used throughout the scientific universe for small-molecule crystallographic data. Each individual crystal structure determination represents one entry in the CSD, denoted by a unique six letter code, the reference code (e.g. SAHYIK for the original MOF-5 structure). Two supplementary digits that may be added identify additional determinations of the same structure and are commonly included for data from different research groups, when done under different experimental conditions or if there is an improved refinement. In the early 2000s, with the improvement of computational capabilities and the conversion of data into connectivity tables, substructure searching at the molecular and the supramolecular level became possible. The resulting structures are now displayed as a two-dimensional diagram as well as in a 3D visualizer. In addition, plentiful crystallographic information together with the literature reference is made accessible.

Hence, the CSD represents an essential tool for researchers in the MOF field, enabling rapid access to data on published structures and related literature. This information greatly facilitates the quest for and design of new materials and the application of reticular chemistry that would otherwise be very difficult.

9.8 Concluding remarks

In summary, we have provided a short introduction to metal–organic compounds, starting from fundamental examples of coordination chemistry dated back to the end of the 19th century. The historical overview covered Werner and Hofmann complexes that enabled fundamental studies based on molecular porous crystals and multidimensional porous networks. Coordination polymers sustained by metal ions connected through organic linkers attracted considerable interest in the 1990s and have led to numerous structures with interesting properties. The utilization of strong bonds, i.e. metal–carboxylate bonds, at the end of the 1990s, represented a turning-point in the field, since it enabled the synthesis of framework materials with structural integrity and permanent porosity. Subsequently, very high surface area MOFs were synthesized, with a capacity that exceeded all other known porous inorganic and organic materials. With respect to the ever increasing interest in metal–organic frameworks throughout the last 15 years, we anticipate a promising and long-lasting future for this relatively new class of material.

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