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Open-framework coordination complexes from hydrogen-bonded networks: toward host/guest complexes

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Abstract

Coordination compounds with peripheral hydrogen bonding substituents have been used to assemble infinite frameworks of one, two, and three dimensions. The propagation of 1D, 2D and 3D network depends on the nature of the metal ion, the number of hydrogen bonding substituents used, and the nature and placement of the hydrogen bonding substituents. An overview of coordination complexes connected via simple hydrogen bonding substituents, e.g. carboxylic acids and carboxamides, is given, and analogous organic and inorganic hydrogen bonding networks are discussed. The use of 2D and 3D hydrogen-bonded coordination networks in creating host–guest networks is also discussed.

Keywords: Crystal structures; Hydrogen bonds; Intermolecular interactions; Host–guest complexes; Crystal engineering; Supramolecular chemistry

1. Introduction

The tools used in organic crystal engineering are hydrogen bonds and other intermolecular interactions [1–5], while those used in coordination polymer chemistry are coordinate-covalent bonds [6–8], but the goal of both disciplines is often the same, i.e. creating 1D, 2D and 3D networks in crystalline solids. So, even though crystal engineering began with efforts to define the role of intermolecular forces in organizing organic molecules and ions in the solid state, perhaps coordination polymer chemistry can be included under the ‘crystal engineering’ umbrella. In fact, coordination chemistry has much to offer a crystal engineer, as there is a wealth of information about the coordination geometries provided by metal ions in a variety of oxidation states, e.g. linear coordination using Ag(I), square planar coordination with Pt(II), octahedral coordination using Ni(II), etc. Thus a 1D, 2D, or 3D coordination network may arise from propagation of the coordination geometry of metal complex ions.

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Recently, the principles set forth by organic crystal engineering, especially regarding the reliability of hydrogen bonds, have been applied to the assembly of coordination networks [5,9–11]. In other words, coordination complexes equipped with peripheral hydrogen bonding substituents have been synthesized, with the intent of finding reproducible assembly strategies.

Many supramolecular chemists and crystal engineers are preoccupied by a quest for space, the goal being to create materials to store molecules or ions, to develop chemical sensors, or to use the channels or cavities as templates for catalysis. In order to *create* space, one must have a strategy for assembly, a basis for generating a host network. One danger is that even if one is successful in creating the desired framework, the networks may themselves occupy intra-net space through interpenetration. In many such cases, the structures are ‘host–host frameworks,’ i.e. they are closely packed and do not provide space for guests. For applications such as storage, sensors, and catalysis, it is preferable to create a host framework in which a guest or guests is trapped. Strategies for the assembly of hydrogen-bonded coordination networks, and for creating host–guest complexes from these networks, are the subjects of this review.

The hydrogen-bonded networks have been organized according to their dimensionality and shape. All frameworks are interconnected via strong hydrogen bonds [12] and coordinate covalent bonds, as these interactions are directional, thus reliable tools for supramolecular assembly. Frameworks assembled mainly through hydrogen bonds to solvents, simple counter-ions, and e.g. aquo and amino ligands [13], typically non-directional in nature, have not been included in this overview (although some exceptions have been made). Hydrogen-bonded organometallic networks have been reviewed elsewhere [14–18]. The crystal structures of all complexes discussed herein have been previously reported.

2. Hydrogen bonds in inorganic crystal engineering

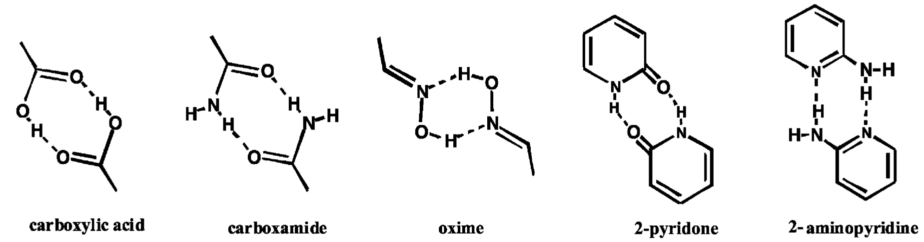
Coordination compounds with peripheral hydrogen bonding substituents can present synthetic challenges to supramolecular chemists who are interested in hydrogen-bonded assembly, since the metal ions may themselves coordinate with the electronegative atoms that are sources of strong hydrogen bond donors and acceptors. In addition, the counter-ions that often escort metal complexes can serve as hydrogen bond donors or acceptors [19–22]. Regardless, it has been found that hydrogen bonding synthons [23] that appear in many organic networks, such as carboxylic acid dimers or amide–amide dimers, can also be useful in inorganic crystal engineering, Scheme 1 (top).

Homomeric, e.g. carboxylic acid–pyridine hydrogen bonds and those between peripheral ligands and a counter-ion (charge-assisted hydrogen bonds) have also been used to connect coordination complex networks, e.g. imidazolium-carboxylate, amino-carboxylate, Scheme 1 (bottom).

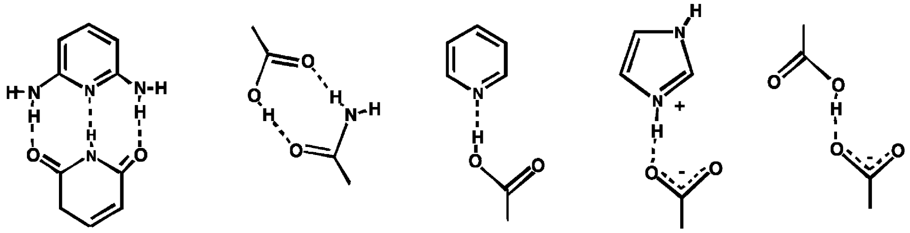
3. 1D Hydrogen-bonded coordination networks

A search of the Cambridge Structural Database [24] yielded an interesting testament to the growing use of peripheral hydrogen bonds in inorganic crystal engineering: a search limited to metal complexes containing two or more

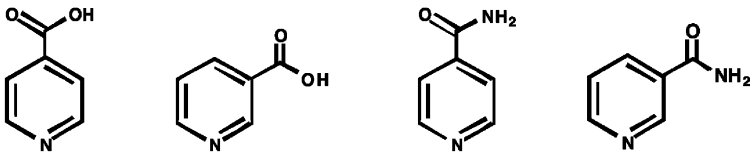
Homomeric hydrogen-bonding synthons



Heteromeric hydrogen-bonding synthons



Scheme 1. Hydrogen bonding synthons.



Scheme 2. The usual suspects. Ligands for hydrogen-bonded coordination complexes, from left: *iso*nicotinic acid, nicotinic acid, *iso*nicotinamide, nicotinamide.

pyridine-based ligands substituted with carboxylic acid or carboxamide in the 3- or 4- position, Scheme 2, shows that before 1994, the combination of two or more of these nicotinic acid or nicotinamide ligands with metal ions had occurred 28 times altogether. But from 1990 through 2001 one can see a significant increase in structures meeting these criteria:

Time frame	Number of structures
1990–1991	3
1992–1993	6
1994–1995	6
1996–1997	11
1998–1999	32
2000–2001	42

Perhaps even more significant is the rise in the number of groups interested in these studies. The 32 structures in 1998–1999 came from only seven groups, but in 2000–2001, over twice as many groups published the 42 structures.

This section outlines pyridine-based and other ligands used to assemble coordination networks of 1D, 2D and 3D.

3.1. Linear and zigzag chains

Linear assemblies may be created by e.g. linear Ag(I)L_2 complexes, square planar Pd(II)$L_2L'_2$, or octahedral Fe(II) $L_2L'_4$, where the two hydrogen bonding ligands, L, are *trans*-configured.

A good example of a linear coordination network connected via carboxylic acid–carboxylate hydrogen bonds is Ag(*iso*nicotinate)(*iso*nicotinic acid) (**1**) Fig. 1 (top) [25]. In this structure, it is clear that not only are the ligands arranged in a near-linear fashion, but so are the hydrogen-bonded substituents. In contrast, a Ag(I) structure in which hydrogen bonding substituents are located at the 3-position on the pyridine ring, for example Ag(6-methylnicotinate)(6-methylnicotinic acid) (**2**) exhibits a zigzag chain through carboxylic acid–carboxylate hydrogen bonds [26]. The zigzag arrangement results from a *trans* orientation of the carboxylic acid and carboxylate substituents, Fig. 1 (middle). One further permutation of these types of complexes is one in which ligand substituents located in the 3-position are arranged in a *cis* fashion in the metal complex, for example in the structure of [Ag(3-aldoximepyridine)$_2$][PF_6] (**3**) Fig. 1 (bottom) [27]. In this case, self-complementary oxime–oxime hydrogen bonds propa-

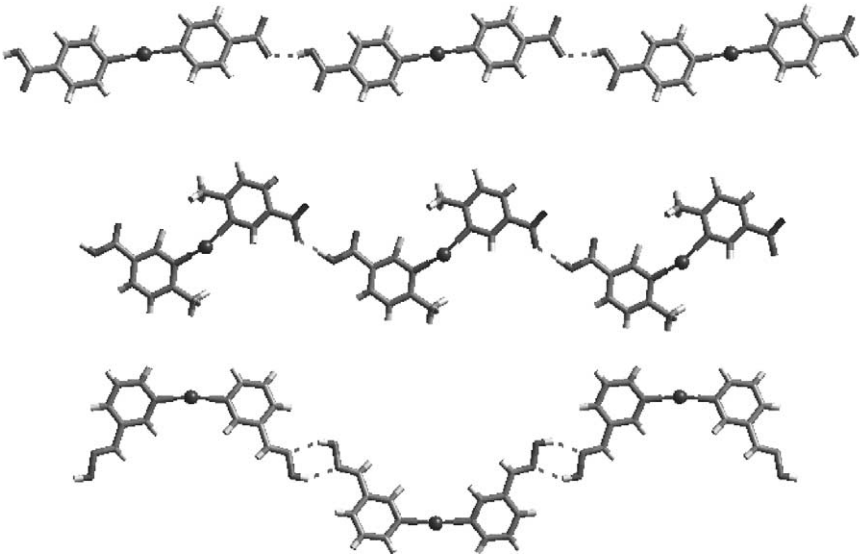


Fig. 1. Straight (top), zigzag (middle), and wavy chain configurations of 1D networks from **1**, **2** and **3**, respectively. Carboxylic acid–carboxylate (**1** and **2**) and oxime–oxime (**3**) hydrogen bonds are shown.

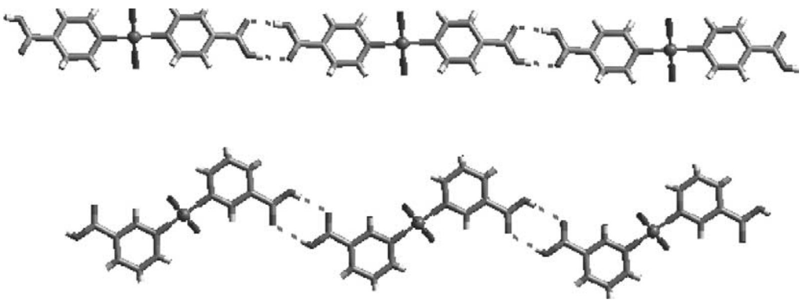


Fig. 2. Linear and zigzag hydrogen-bonded chains from carboxylic acid dimers in **4** and **5**.

gate the 1D network, with the overall motif being a wavy chain.

For square planar complexes, an additional structural variable comes from ancillary ligands, ligands not involved in strong hydrogen bonds, which may have either a *cis* or *trans* relationship. For example, $PdCl_2$(*iso*nicotinic acid)$_2$ (**4**) exhibits a *trans*-arrangement of chloride ligands, and therefore a *trans*-arrangement of the pyridine-based ligands as well [28]. With the linear relationship of peripheral carboxylic acid substituents, a 1D network results from head-to-head carboxylic acid dimers, Fig. 2 (top). A *trans* nicotinic acid complex, $PdCl_2$(nicotinic acid)$_2$ (**5**) exhibits a similar hydrogen bonding pattern [28], but the chains are now in a zigzag arrangement due to the 3-position of the carboxylic acid substituents, Fig. 2 (bottom). Ligands with peripheral oxime substituents, coordinated to Pd(II)(I)$_2$ through cyano groups in *trans*-PdI_2(1-cyano-2,6-diisopropyl-4-phenyloxime)$_2$ (**6**) also take part in self-complementary oxime–oxime hydrogen bonds, yielding a linear chain [29].

Cis-complexes of square planar Pd(II) or Pt(II) can be synthesized using non-chelating ligands [30], as in the case of [Pt(*iso*nicotinamide)$_2$(PEt_3)$_2$][NO_3]$_2$ (**7**). The hydrogen-bonding network is a 1D zigzag chain, as the cationic metal complexes are interconnected through head-to-head amide–amide interactions Fig. 3 (top). The phosphine ligands alternate along the chain. A similar metal complex, [Pd (nicotinamide)$_2$(PPh_3)$_2$][O_3SCF_3]$_2$ (**8**) is interconnected through amide–amide hydrogen bonds [31], but in this case the phosphine ligands are located on the same side of the chain throughout, resulting in a near-linear chain,

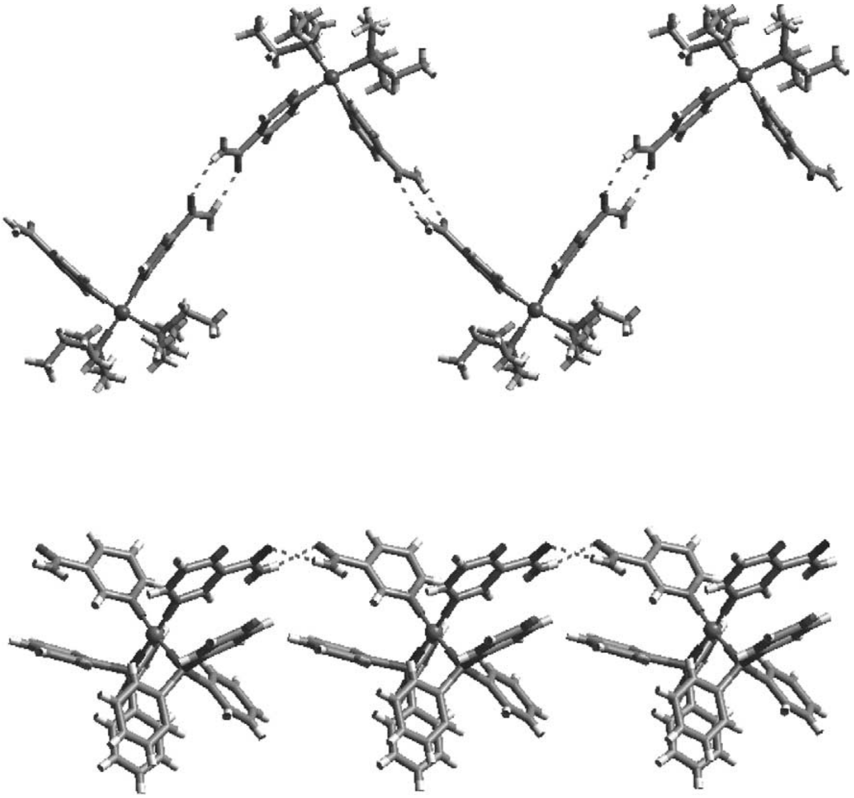


Fig. 3. Zigzag and linear hydrogen-bonded chains of *cis* Pt(II) and Pd(II) complexes **7** and **8**.

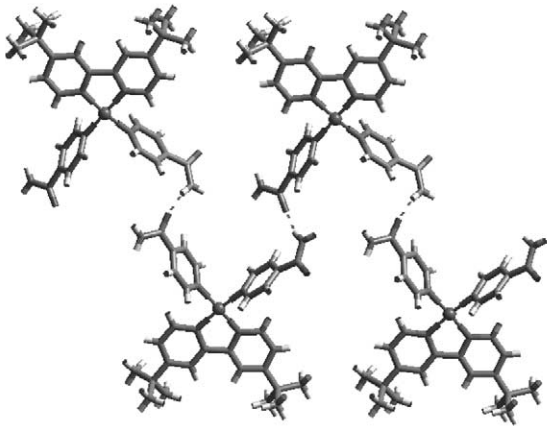


Fig. 4. Wavy chain resulting from catemeric amide–amide hydrogen bonding in **9**.

even with a *cis* arrangement of hydrogen bonding ligands, Fig. 3 (bottom). These two compounds illustrate that while their complex ions are in some ways quite similar, there is a large difference in the supramolecular attributes of **7** and **8**. The former exhibits a hydrophobic periphery, while the latter chain has two distinct sides, one hydrophobic and one hydrophilic, so that each chain in **8** contains a polar axis perpendicular to the direction of propagation of the chain.

Another option for 1D chain design is the use of bis-chelating ancillary ligands to lock the hydrogen bonding ligands into a *cis* arrangement. For example, Pd(5,5′di-*t*-butyl-2,2′bipyridyl)(*iso*nicotinamide)$_2$ (**9**) interconnects through catemeric amide–amide interactions to create wavy chain [31], rather than the zigzag chain found in **7**. So like **7**, the chain has a hydrophobic periphery, but the distance between the metal ions is significantly reduced, Fig. 4.

An elegant example of the use of synthetic methods to effect supramolecular change is that of *iso*nicotinamide-substituted Re$_6$(μ_3-Se)$_8$ di-cationic clusters [32]. The clusters are modified with PEt$_3$ ligands as well as either *trans*- (**10**) or *cis*- (**11**) related *iso*nicotinamide ligands. The supramolecular arrangement is influenced by head-to-head amide–amide hydrogen bonds, yielding linear and zigzag chains, respectively, Fig. 5.

3.2. Ladders and ribbons

Some 1D networks are not made up of simple chains, instead chains may cross-link to create a ladder motif. Both the Ag(I) and Pd(II) systems described in Section 3.1 also exhibit ladder motifs in some instances. One example is [Ag(nicotinamide)$_2$][O$_3$SCF$_3$] (**12**) in which a ladder motif persists, Fig. 6 (top) [33]. This motif results from two attributes of the complex ion. First, unlike carboxylic acid, the amide moiety contains an extra hydrogen bond donor, and can therefore enter into the dual-role hydrogen bonding pattern. Second, this is another example of a *cis* orientation of the peripheral substituents, which leads to a 1D motif. A similar motif is observed in a *cis* Pd(II) complex, [Pd(bis(diphenylphosphino)methane)(*iso*nicotina-

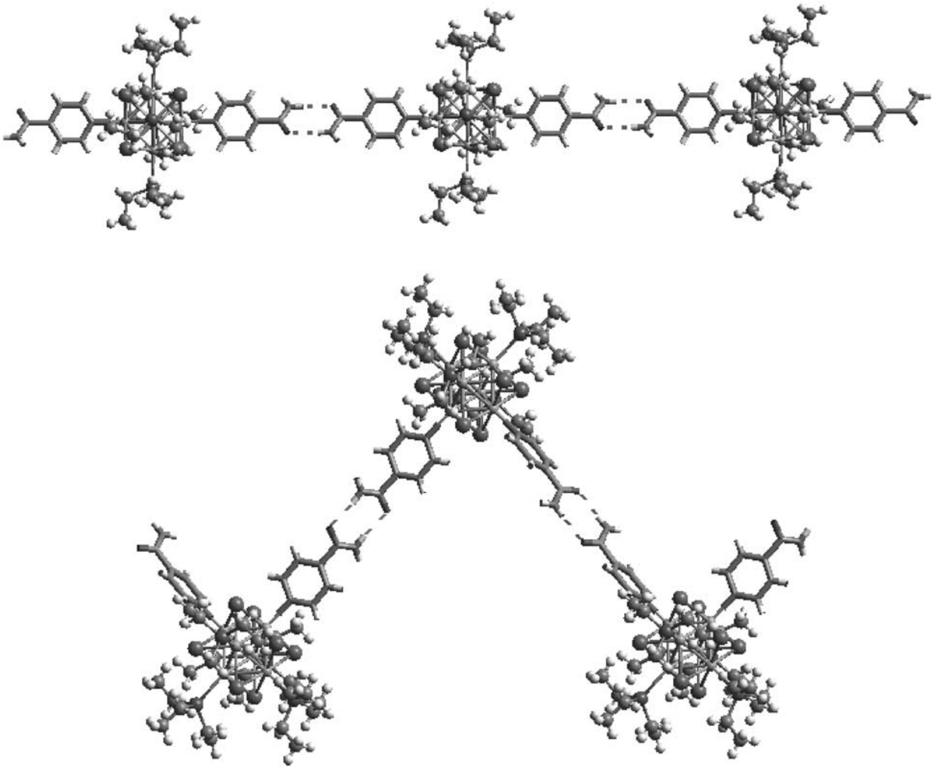


Fig. 5. Linear vs. zigzag configuration in *iso*nicotinamide-substituted [Re$_6$Se$_8$]$^{2+}$ clusters **10** and **11**.

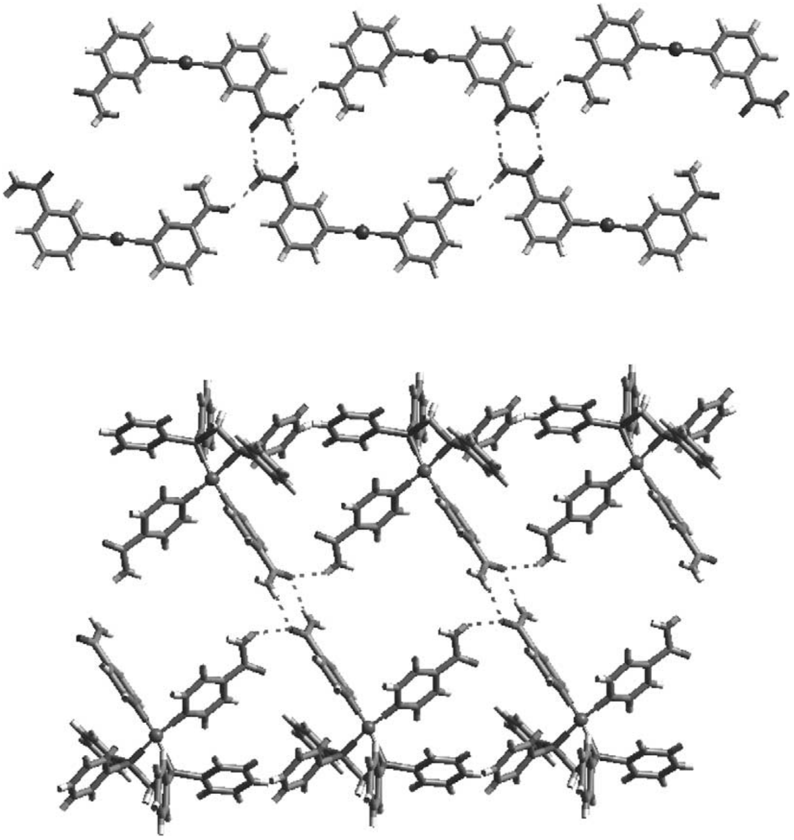


Fig. 6. Hydrogen-bonded ladders via amide–amide hydrogen bonding in Ag(I)-containing **12** and Pd(II)-containing **13**.

mide)$_2$][O_3SCF_3]$_2$ (**13**) Fig. 6 (bottom) [31]. The supramolecular arrangement for both compounds is that of a ladder with a hydrophobic periphery and a hydrophilic interior.

In some instances, even a square planar metal complex containing four hydrogen-bonded ligands may exhibit a 1D hydrogen bonding pattern, as in the case of [Pt(nicotinamide)$_4$][Cl]$_2$ (**14**) in which the nicotinamide rings are arranged parallel in the solid state, and connect through ribbons of head-to-head amide–amide hydrogen bonds [34].

4. 2D Hydrogen-bonded coordination networks

Grid-like or lamellar 2D networks can result from e.g. square planar, octahedral, or even linear metal complexes. For example, it has been found that linear Ag(I) nicotinamide complexes can interconnect in 2D arrangements when the two amide moieties are *trans* and exhibit catemeric ligand–ligand hydrogen bonding, as in [Ag(nicotinamide)$_2$][PF_6]$_2$ (**15**) Fig. 7 (top) [33]. Chemically, the metal cation is identical to those that show ladder-type 1D hydrogen bonding (Section 3.2), but the supramolecular arrangement was found to be dependent on the nature of the counter-ion. Spherical counter-ions such as BF_4 and PF_6 lead to the sheet-like 2D arrangement, and asymmetric counter-ions such as triflate give the ladder arrangement. A virtually identical hydrogen bonding pattern is observed in $PdCl_2$(N'-methylnicotinamide)$_2$ (**16**) Fig. 7 (bottom) [31]. In this case, metal complexes that are quite different, e.g. 2-coordinate vs. 4-coordinate, cationic vs. neutral, exhibit similar supramolecular behavior.

A 2D sheet is also found when two bis-chelating hydrogen malonate (Hmal) ligands are used in an octahedral metal complex, Co(H_2O)$_2$(Hmal)$_2$ (**17**) [35]. Here, malonate ligands coordinated to the metal center through the oxygen atoms of both the carboxylic acid and the carboxylate moieties, and carboxylic acid–carboxylate hydrogen bonds connect the complexes into sheets.

2D Motifs can also be produced using three or more hydrogen bonding ligands. For example, [Pt(*iso*nicotinamide)$_4$][PF_6]$_2$ (**18**) interconnects through both catemeric and head-to-head hydrogen bonds [34], similar to those in the Ag(I) and Pt(II) ladder complexes discussed in Section 3.2. In this example, the non-hydrogen bonding ancillary ligands have been replaced by ligands that can participate in hydrogen bonding interactions, which results in an infinite 2D assembly rather than the 1D ladder motif found in **13**.

Octahedral metal complexes are also suitable for 2D assemblies, especially if they contain four hydrogen bonding ligands in one coordination plane, e.g. [Ni(*iso*nicotinamide)$_4$(H_2O)$_2$][ClO_4]$_2$ (**19**). Here, each ligand is involved in two catemeric amide–amide interactions, leading to a 2D ar-

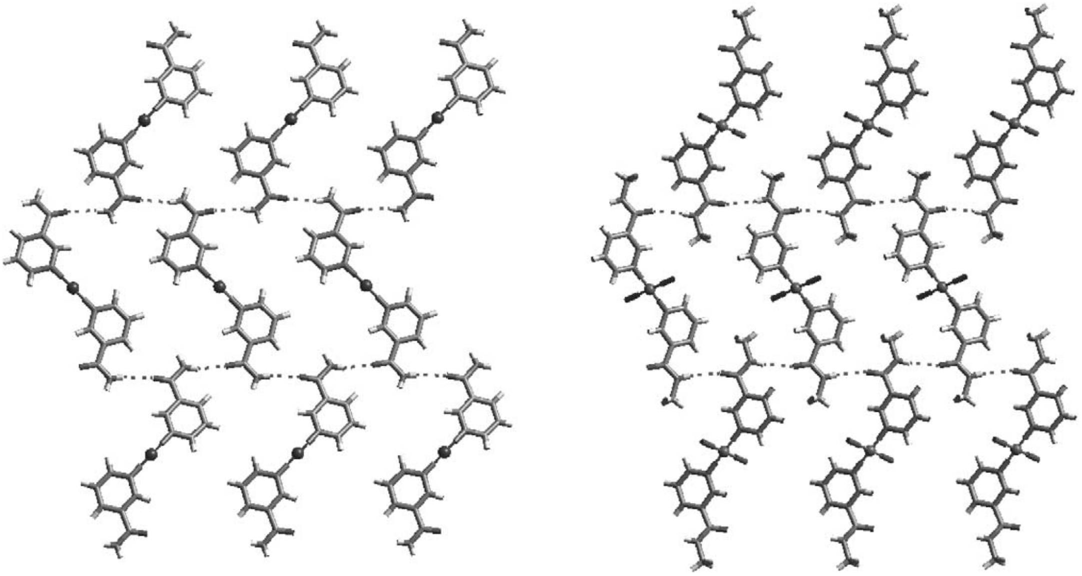


Fig. 7. 2D Sheets propagated via catemeric amide–amide hydrogen bonding in Ag(I)-containing **15** and Pd(II)-containing **16**.

rangement, Fig. 8. Other examples include Co(II) and Zn(II) complexes of amino-pyrimidine-substituted terpyridine ligands, which create grid-like structures [37].

Cluster compounds modified with hydrogen bonding ligands are also discussed in Section 3.1, but perhaps the first such system was oxo-benzamide substituted $[Mo_6Cl_8]^{4+}$ clusters, $[Mo_6Cl_8(\text{4-oxobenzamide})_6]^{2-}$ (**20**) [38]. In this example, the crystal structure of the sodium cryptand salt of **20** demonstrates how classic amide–amide ribbons can create 2D sheets, Fig. 9.

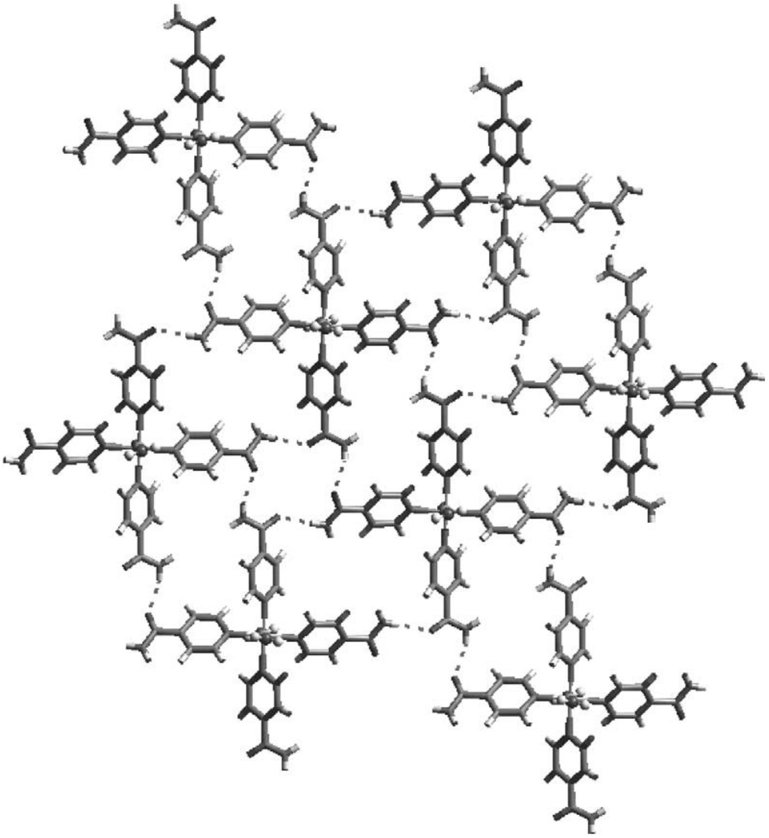


Fig. 8. Amide–amide hydrogen-bonded sheet in octahedral Ni(II) complex **19**.

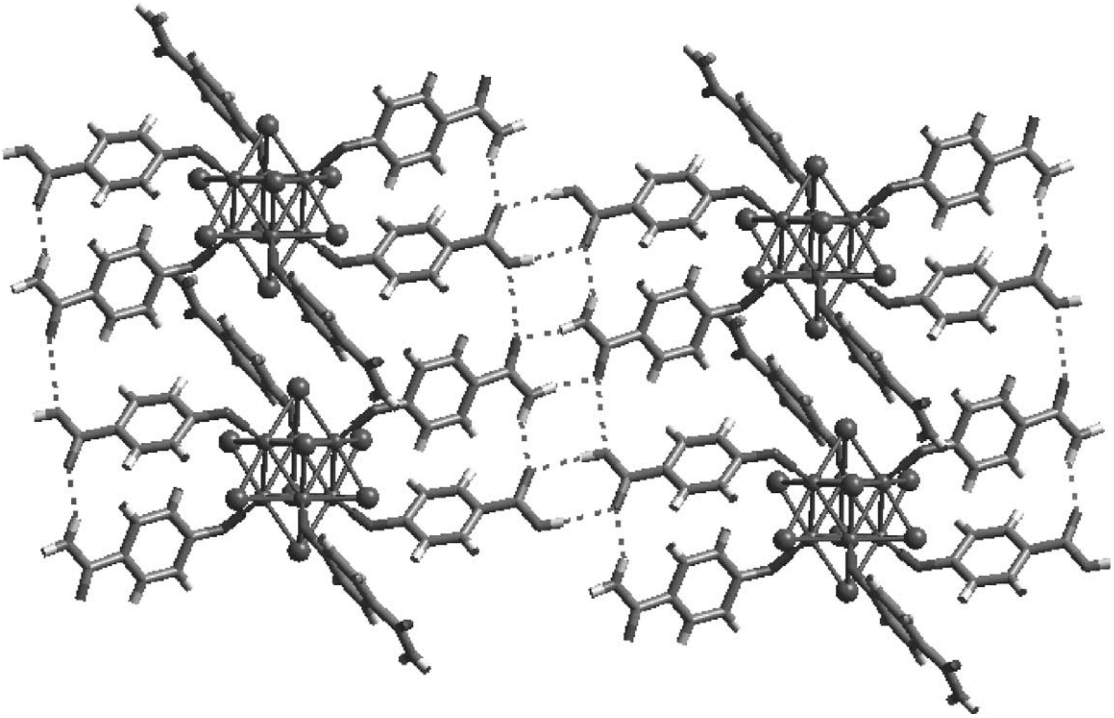


Fig. 9. 2D Arrangement of $[Mo_6Cl_8]^{3+}$ clusters via amide–amide hydrogen-bonded ribbons in **20**.

5. 3D Hydrogen-bonded coordination networks

There are relatively few examples of 3D networks assembled through ligand–ligand hydrogen bonds. One example is three-coordinate $[Ag(\textit{iso}nicotinamide)_3]^+$ (**21**) which crystallizes as either the perchlorate or tetrafluoroborate salt [39]. The geometry at the metal center is approximately trigonal, and catemeric hydrogen bonds between neighboring cations result in a 3D net that closely mimics that of $ThSi_2$, Fig. 10. The networks are porous, but are filled with crystallographically equivalent nets, creating a host–host, instead of a host–guest, 3D structure.

Some of the first 3D hydrogen-bonded coordination complexes were based on $[Cu(3\text{-cyano-6-methyl-2-pyridinone})_4]^+$ (**22**) [11]. In these examples, the ligand coordinates to the metal ion through the cyano group, and intermolecular hydrogen bonding takes place through the pyridone group. The tetrafluoroborate and perchlorate salts of these complexes exhibit catemeric pyridone–pyridone hydrogen bonds, resulting in square channels that contain the counter-ions. Increasing the counter-ion size by using hexafluorophosphate or triflate anions results in head-to-head pyridone–pyridone hydrogen bonds, and a diamondoid framework, Fig. 11. The networks are similar to those found in the organic diamondoid lattices of Wuest and co-workers, where diaminotriazines are the source of hydrogen bonds [40]. The latter complexes have been found to contain neutral guest molecules, with over 60% of the volume taken up with guest species in extended systems, even after interpenetration [41]. However, the Cu(I)-pyridone solids based on **22** contain only counter-ions in the channels or voids.

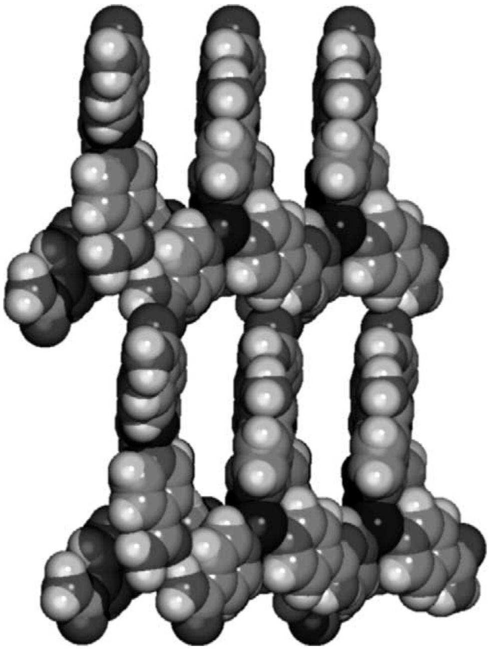


Fig. 10. Space filling representation of one 3D hydrogen bonding network in **21**.

6. Hydrogen-bonded coordination networks as hosts

It has been difficult to develop reproducible strategies for creating hydrogen-bonded host–guest systems, especially due to the tendency for framework interpenetration [42].

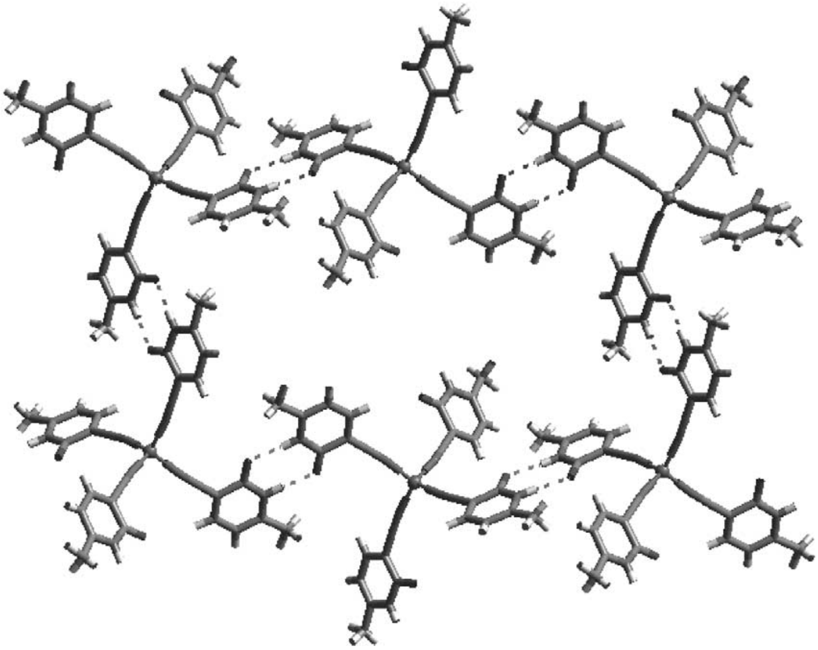


Fig. 11. Part of the 3D hydrogen-bonded diamondoid network in **22**.

Several methods have been used to try to effect creation of space in host lattice, for example varying the solvent of crystallization, templating using large guest molecules, and synthesizing extended ligands so that space remains even after interpenetration. Unfortunately, there is no way to guarantee a system in which interpenetration does not occur. But fortunately, this has not prevented crystal engineers from trying, and some examples of host–guest compounds are reported in this section.

6.1. 2D Host networks

In some cases, the formation of large pores or channels depends on the presence of large counter-ions. One such example involves the cryptand- or crown-encapsulated potassium salts of octahedral $[Ni(Hbim)_3]^-$ (where Hbim is a negatively charged bi-imidazole ligand) [43]. The pseudo-hexagonal networks leave much space, created through self-complementary HBim hydrogen bonds, Fig. 12. The

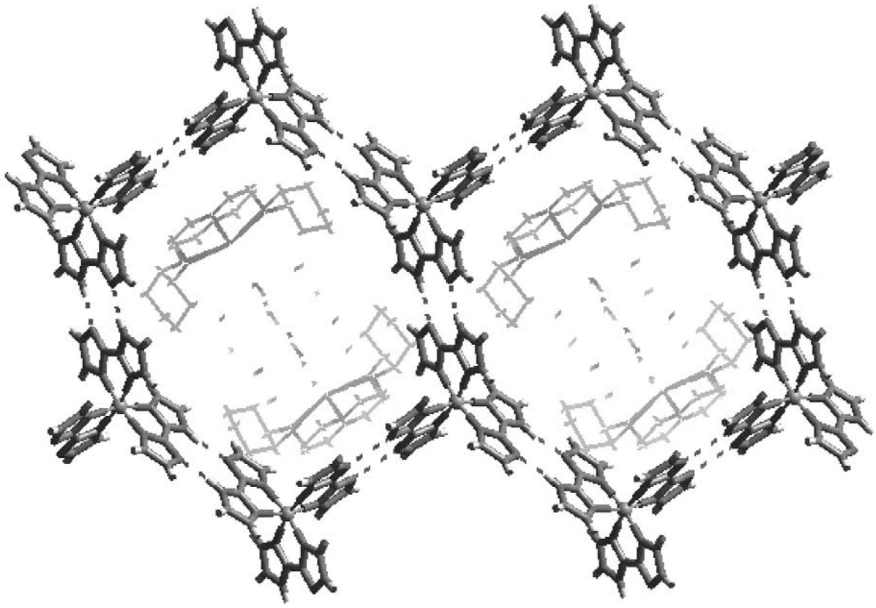


Fig. 12. $Ni(Hbim)_3$ hydrogen-bonded layer (dark gray), with crown-encapsulated potassium cations (light gray) and additional solvent molecules in center of channels, reported in Ref. [43].

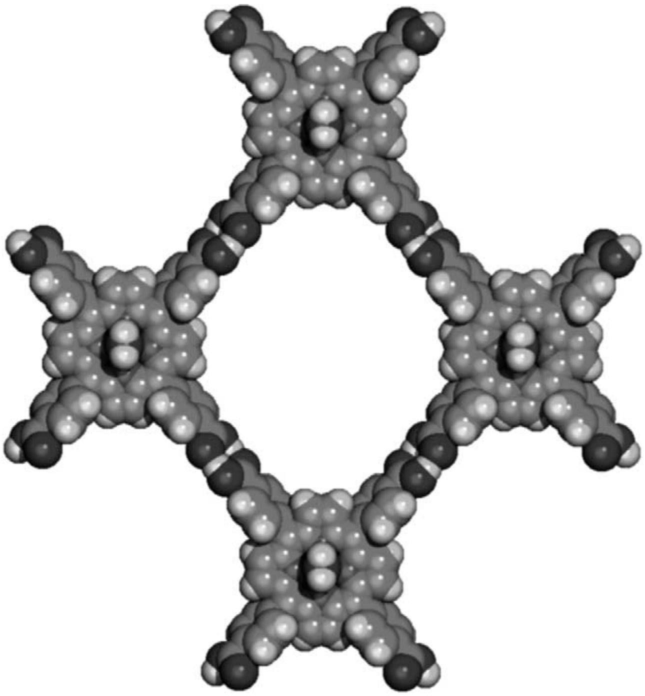


Fig. 13. One square of the infinite square-grid hydrogen-bonded network in a 4-phenylcarboxylic acid-substituted Zn(II)-porphyrin, reported in Ref. [48].

large, templating counter-ions occupy most of the channels created in the structure. Much of the 'guest' in this case is actually the counter-ion, but space remains for solvent channels.

One extensively studied 2D host system is that of porphyrins containing peripheral hydrogen bonding substituents. Zn(II) porphyrin complexes suitable for crystal engineering have been synthesized by Goldberg and coworkers [44], and include carboxylic acid- [45], carboxamide- [46], and diaminotriazine-substituted porphyrins [47]. One carboxylic acid structure, in which porphyrin units are interconnected at all four corners via carboxylic acid hydrogen-bonded dimers, form overlapping porphyrin grids, Fig. 13. The resulting 1.5 nm channels, 61% of the crystal volume, are partially-filled with solvent molecules [48]. An Fe(III) porphyrin with similar phenyl-carboxylic acid substituent, formed a nearly identical network [49]. In this case the grids overlap slightly, so that 44% of the volume is taken up by solvent-containing channels, with two acetic acid molecules and four water molecules per porphyrin unit. The crystals are not stable outside of the mother liquor.

A grid-like assembly is also found in [Pt(*iso*nicotinamide)$_4$][Cl]$_2$·4*iso*nicotinamide (**23**) [36]. In **23**, the ligand–ligand hydrogen bonding is through head-to-head hydrogen bonds in 1D only. Amide–chloride hydrogen bonds create a 3D network. Regardless, it is worth noting that a large percentage of the crystal volume is occupied by hydrogen-bonded guest *iso*nicotinamide molecules. The oxime substituents on [Ni(4-aldoximepyridine)$_4$][Br]$_2$·2(4-aldoximepyridine) (**24**) serve to interconnect the metal-containing cations into a grid-like assembly [36]. While the pores in the grid have the shape of an hourglass, the arrangement of neighboring grids is staggered, so that the size of the channels is significantly reduced, Fig. 14. Still, additional non-coordinated 4-aldoxime pyridine molecules are located in the channels, and the structure is stabilized by cation–anion oxime–bromide hydrogen bonds.

Another hydrogen-bonded host–guest complex arose from a desire to make a neutral metal complex, therefore eliminating the structural interruptions of a counter-ion. Pt(*iso*nicotinate)$_2$(*iso*nicotinic acid)$_2$ (**25**) was found to create square grids, propagated through carboxylic acid–carboxylate hydrogen bonds [36]. Extensive interpenetration of the nets does not lead to a close packed structure, instead channels with a diameter of 5 Å contain solvent molecules.

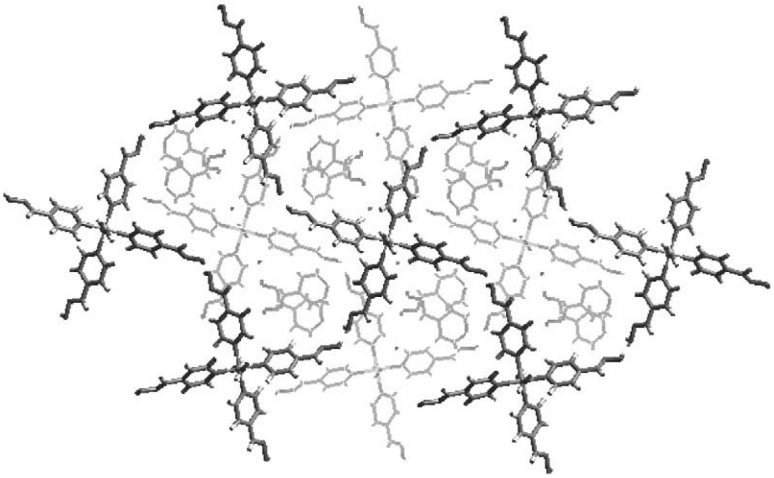


Fig. 14. Part of the 3D structure of **24**. Dark gray metal complexes represent one hydrogen-bonded layer. Light gray metal complexes are crystallographically-equivalent layers below. Additional 4-pyridine aldoxime molecules (light gray) reside in channels.

6.2. 3D Host networks

One of the first 3D hydrogen-bonded coordination networks was published relatively early, in 1995, [50], and it also happens to be a host network. From a coordination chemistry perspective, the structure is a cousin of the $Ni(Hbim)_3$ structures discussed at the beginning of this section, since there are three bis-chelating ligands involved. In this case, octahedral Co(III) ions are coordinated to three equivalents of 2,2′-bipyridyl-5,5′dicarboxylic acid (H_2dcbpy) through the bipyridyl nitrogen atoms. The resulting neutral complex, $Co(Hdcbpy)_3$ (**26**) contains three mono-deprotonated ligands. The 3D grid network, Fig. 15, is propagated via carboxylic acid–carboxylate interactions. In this structure there are two interpenetrating lattices of opposite chirality but small channels remain, which are filled with solvent molecules.

6.3. Host networks from metal ions and organic counter-ions

2D Coordination networks have been synthesized by Hosseini and coworkers [51], in which simple, hexacoordinate metal-cyano trianions are connected to amidinium counter-ions through hydrogen bonds. Both $[Co(CN)_6]^{3-}$ and $[Fe(CN)_6]^{3-}$ were used to create the 2D networks, which are organized such that channels filled with water exist throughout the structure.

A similarly-shaped metal cation, $[Co(NH_3)_6]^{3+}$, in combination with disulfonate anions 1,4-piperazine-bis(ethanesulfonate) or 2,6-naphthalenedisulfonate, create 3D hydrogen-bonded hosts [52]. These compounds are particularly noteworthy because they are an inorganic version of the well-studied guanidinium-sulfonate layered solids [53]. In both the organic and the inorganic systems, the C_3 symmetric sulfonate anion hydrogen bond acceptors, and amine-based hydrogen bond donors (guanidinium cation or $[Co(NH_3)_6]^{3+}$) interact to create layered compounds, Fig. 16. The inorganic inclusion solids, which are held together by a 3D hydrogen-bonded network, incorporate water molecules and/or dioxane guest molecules in the lattice.

6.4. Host networks from coordination polymers and hydrogen bonding ligands

Another strategy for assembly of coordination complexes depends on the combination of coordination polymers and hydrogen bonds. An advantage to this approach is that the coordination polymer networks add strength and thermal stability to the solid. One such example comes from Goldberg and coworkers, in which a 2D porphyrin network (see Section 6.1) is combined with 4,4′-bipyridyl (4,4′-bpy) axial ligands [54]. 1D stacks of porphyrin molecules, linked via bridging 4,4′-bpy, are further inter-connected in the remaining 2D through hydrogen bonds, resulting in a 3D assembly. Solvent molecules occupy 53% of the crystal volume.

A strategy based on hydroxy-substituted binaphthalene dicarboxylic acids has led to 2D and 3D networks of 1D coordination polymers. Co(II), Cd(II), and Mn(II) coordinated to the carboxylate moieties to create 1D coordination

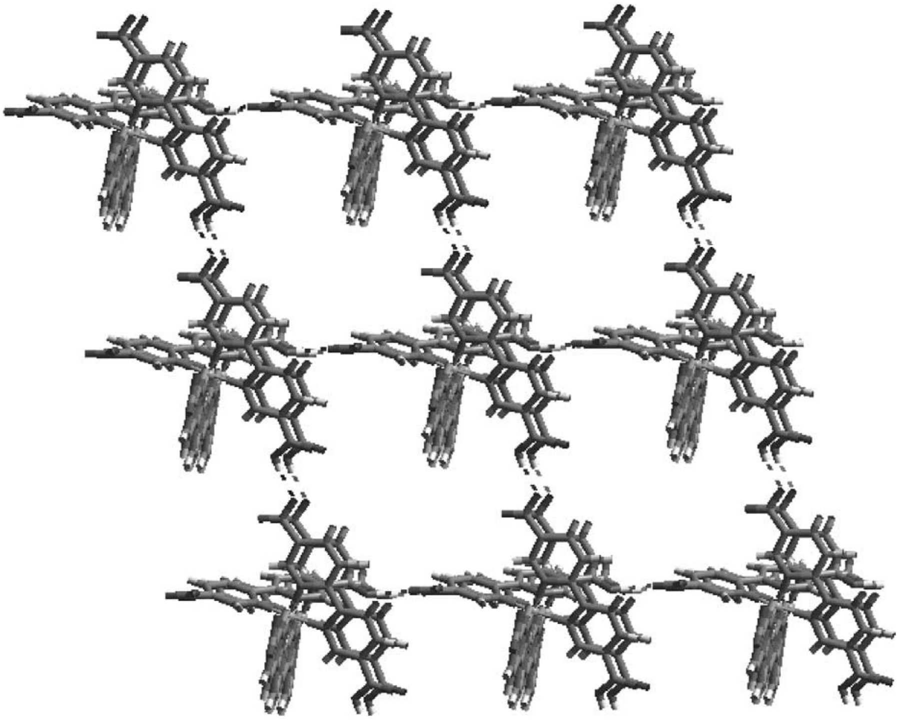


Fig. 15. One of two 3D hydrogen-bonded interpenetrating nets in **26**. Interpenetration reduces but does not eliminate channel space.

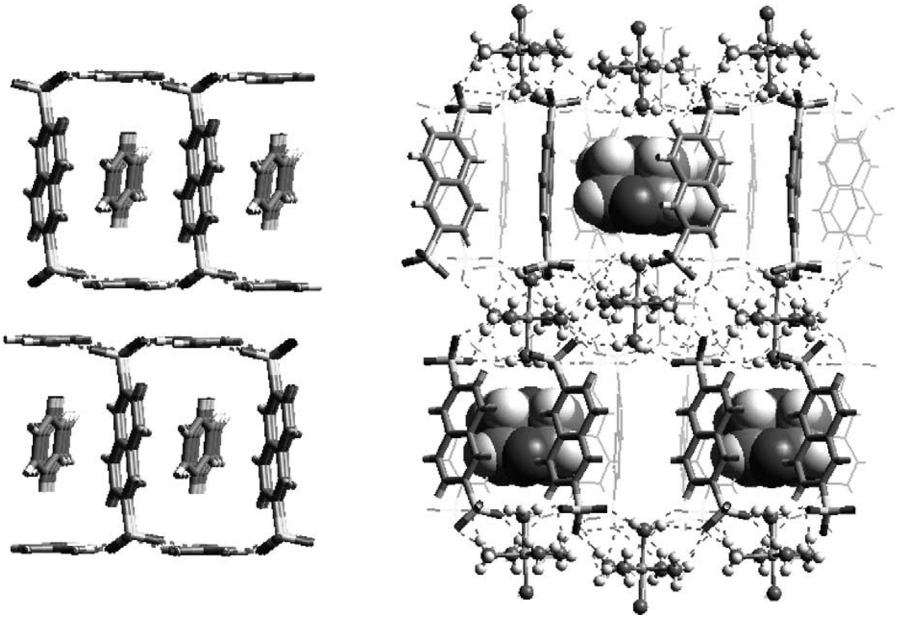


Fig. 16. Organic guanidinium-sulfonate host–guest structure (left) and inorganic $[Co(NH_3)_6]^{2+}$ -sulfonate host–guest structure (right). The disulfonate pillar is the same in both structures.

polymers, and hydroxyl–hydroxyl hydrogen bonds yield either 2D or 3D networks, with up to 59% of void space in the crystal structure [55]. Pyridine-based ligands with hydrogen bonding substituents have been used in conjunction with coordination polymers as well. One such study was reported by Sekiya and Nishikiori [56], who demonstrate that a combination of Ni(II)-thiocyanate coordination polymers, *iso*nicotinic acid and derivatives thereof, and in some examples neutral diacid hydrogen-bonded linkers, can provide the space needed for hosting neutral aromatic guests such as pyrene, 9,10-dichloroanthracene, phenanthrene, benz[*a*]anthracene, coronene, perylene, and naphthacene, Fig. 17. Similarly, a 1D $Cd(SCN)_2$ coordination polymer combined with nicotinic acid ligands can build 2D frameworks via carboxylic acid dimers, where nicotinic acid is incorporated as a guest [57].

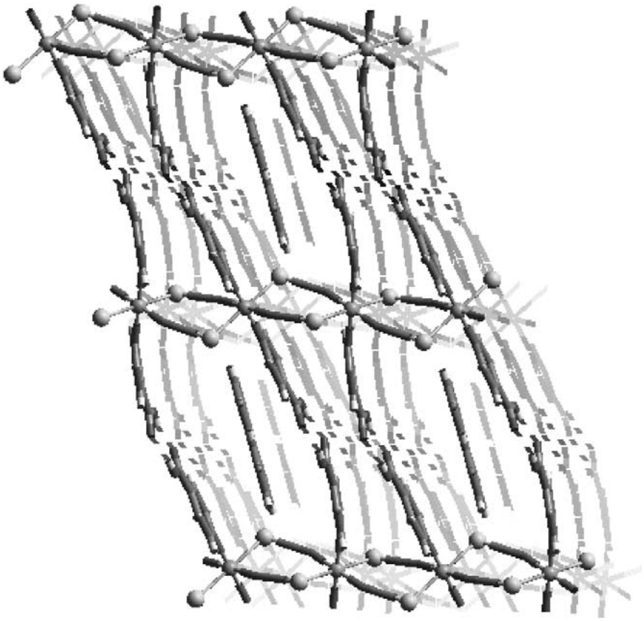


Fig. 17. 1D $Cd(SCN)_2$ coordination polymer connected via carboxylic acid dimers, reported in Ref. [57].

7. Conclusion

The results of the many studies outlined in the review allow us to address questions that might naturally be asked about hydrogen-bonded coordination networks.

First, do the synthons identified from the continuing research in organic crystal engineering also apply to the assembly of coordination networks? Remarkably, the answer is yes! Many metal complexes with peripheral carboxamide substituents exhibit patterns (head-to-head, catemeric, amide–amide ribbons) that are also found in organic systems. Carboxylic acid–carboxylate hydrogen bonds persist as well, and so do many other common synthons. It is not necessary (although it does not hurt!) to use triply complementary hydrogen bonding substituents to create infinite networks of coordination complexes. In organic crystal engineering, motifs may be interrupted by interactions with e.g. solvents and counter-ions, so it is not surprising that the same challenges present themselves in attempting the predictable assembly of coordination complexes. Ligand–ligand hydrogen bonding can be interrupted by counter-ions, non-directional ligands such as water and amines, and solvents. Even the metal center itself can coordinate to a ligand intended for peripheral hydrogen bonding. There is no guarantee, but there are many, many examples where ligand–ligand interactions prevail.

Can we create 1D, 2D and 3D coordination networks from peripheral hydrogen bonding substituents? Again, the answer is yes! Through judicious choice of the coordination geometry, the ligand geometry, and the number, type and placement of the substituents, the chances of achieving the desired network are increased. Especially due to steric constraints (and perhaps for lack of trying) the number of 3D coordination networks remains quite small, and certainly the reliable formation of 3D networks is needed in order to develop the potential for host–guest systems. The study of 3D *organic* networks has already demonstrated that reproducibility and thermal stability can be quite high in these complexes, and perhaps we can look forward to similar developments in the future of hydrogen-bonded coordination networks.

The complexes discussed here demonstrate that advances have been made through systematic studies of hydrogen-bonded coordination complexes. We now have some control over the distances between metal centers [58], and their relative arrangement in the solid state. Methods of obtaining 1D vs. 2D networks have been developed. Linear complexes with distinct hydrophobic and hydrophilic regions can also be constructed rationally. All of these structural characteristics have implications for materials design, and it will be exciting to watch as applications of these materials develop.

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