

Soft organic and metal-organic frameworks with porous architecture: From wheel-and-axle to ladder-and-platform design of host molecules

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The family of wheel-and-axle host molecules is reviewed and the approaches to the creation of new host geometries for supramolecular materials based on weaker interactions are discussed. The combination of bulky groups (or platforms) and spacers yields various host geometries including humming-top molecules (Werner complexes, metal dibenzoylmethanates and other bis-chelates, dimeric metal carboxylates and macrocyclic complexes), wheel-and-axle and dumb-bell shaped molecules and their modifications, ladder-and-platform, shish-kebab, multi-decker, stair-case and double-strand ladder-and-platform oligomeric and polymeric structures. The host shapes are compared with cyclic and trifoil (trityl) host types. The use of metal centers, chelating and macrocyclic ligands (β -diketones, carboxylic acids, Schiff bases, porphyrins, phthalocyanines, corroles, annulenes and their analogs), bridging ditopic ligands and other building elements in the engineering of host molecules is illustrated. The role of such factors as size and nuclearity of the platforms, rigidity/flexibility of the spacers and hydrogen bonding is discussed. The relation between porosity and packing efficiency, predisposition to self-inclusion, parallel alignment and interdigitation, dimensionality and secondary assembly of host molecules in the crystal is examined. Clathration and sorption abilities and other important qualities and functionalities of the new host materials are elucidated.

KEYWORDS: Supramolecular chemistry; crystal engineering; metal complexes; microporosity; organic zeolites; weak interactions; coordination polymers; MOFs; inclusion compounds; Werner clathrates.

Introduction

The design of soft supramolecular materials (SSM)^{1–3} is a modern direction in materials science which exploits new ideas brought forward by supramolecular chemistry and crystal engineering.⁴ In the focus of this paper are SSM formed

as a result of bulk supramolecular assembly of molecular species into a regular structure, with weaker interactions governing the structure and properties of the resulting solids. These solids display a number of remarkable useful properties such as easy conversion from one structure to another and active response to external stimuli.

Specifically, this review is devoted to the design of molecular species (“host”) which will assemble into porous structures in the presence of neutral molecules of another component (“guest”). The resulting supramolecular

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phases, usually called “inclusion compounds” or “clathrates,” may retain their structure, change or collapse upon guest removal, exchange and replacement, depending on the stability of a host framework.^{5–7} Because for the majority of known inclusion compounds the stability of their host frameworks is unknown, these frameworks will be called “porous” *a priori*, with a special reference made to materials whose host framework stability was deliberately studied.

Packing efficiency and inclusion phenomenon

The formation of molecular crystals follows certain rules. Two approaching molecules tend to adopt energetically most favorable mutual arrangement defined by the balance of attractive and repulsive forces. Optimal interatomic distances depend on the participating atoms, their effective charge, and the type of interatomic interaction. The latter varies from such specific and local interactions as coordinative and hydrogen bonds to universal van der Waals interactions.^{8b} All these forces have a potential to organize a set of molecules into the crystal, or giant “supermolecule,” a special arrangement that corresponds to an energetic minimum of the multimolecular system.

The mutual arrangement of molecules in a crystal defines its packing efficiency expressed quantitatively through “packing coefficient” (the fraction of space in a given crystal occupied by molecules represented as combinations of atomic spheres).^{8a,9a} Crystals based on van der Waals interactions have surprisingly similar and relatively high packing coefficients, mostly in the range of 0.65–0.77^{8a} with a minimal value of about 0.6.^{9b} The lower the ability of the molecules to pack densely, the greater their propensity to form amorphous, glassy or, if suitable “guest” species available, inclusion solids. Therefore, the creation of potentially porous molecular frameworks may be based on the design of host molecular geometries that do not conform with the requirement of close packing.

It is necessary to mention that although the focus of this review is on the host molecules, guest species are also active participants in the formation of porous architectures. Different guest species may contribute to a greater or lesser extent to the formation of a desired architecture or may facilitate different crystal structures, with such factors as multi-point recognition between guest and host¹⁰ and guest-to-host symmetry relation¹¹ having been traced in the literature. Moreover, the identification of a suitable guest may help to crystallize big irregular-shaped molecules¹² or stabilize unusual host molecular species.^{1–3}

It seems relevant here to mention three families of host geometries (Fig. 1). (1) Cyclic molecules exhibit or may adopt the shape of ring, with void space already available in the center of the molecule. In the solid, these voids may form individual capsules for guest species or may combine into a system of channels. The best known classes of cyclic host molecules are cyclodextrins (Fig. 1a),¹⁶ calixarenes,¹⁷ cyclophanes^{18c,19} and cyclic peptides.^{20,21} (2) “Trifoil” molecules have three planar fragments connected in a single point.^{18a,22a} The simplest representative, triphenylmethane (Fig. 1b), forms guest-free orthorhombic structure with packing coefficient of 0.6.^{9b} Alternatively, it may form another, trigonal structure with voids filled by guest species and having higher packing efficiency.^{9a,23} (3) The third family comprises molecules combining bulky (or planar) groups and bridging “rods.” Typical representatives are so-called “wheel-and-axle” host molecules;^{22b} (Fig. 1c) the name will be used for the whole family in the further text. This third family of host geometries is reviewed in the present paper.

The family of wheel-and-axle host geometries

Basic geometries are summarized in Fig. 2. Humming-top geometry comprises one plane penetrated with one rod (Fig. 2a). The ends of the rod may be finished with bulky or flat groups or may contain functionalities facilitating a predefined

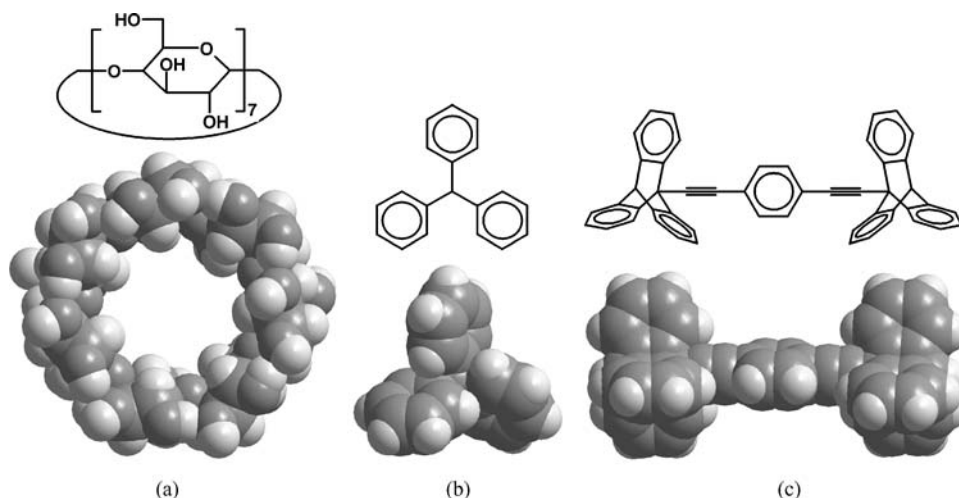


Fig. 1. Representatives of cyclic (β -cyclodextrin)¹³ (a), trifoil (triphenylmethane)¹⁴ (b) and wheel-and-axle (1,4-bis(2-(9-triptycyl)ethynyl)benzene)¹⁵ (c) host molecules. Space-filling models outline van der Waals dimensions.

assembly in the crystal. Wheel-and-axle architecture comprises two bulky fragments connected by a bridging spacer (Fig. 2b,c,d). The bulky fragments may have various shapes, such as wheels (Fig. 2b), squares (“H-shaped molecules”), cones (Fig. 2c) or ellipsoids (“dumb-bell geometry”, Fig. 2d). The bridging spacer may vary in shape and be either rigid or flexible. Finally, ladder-and-

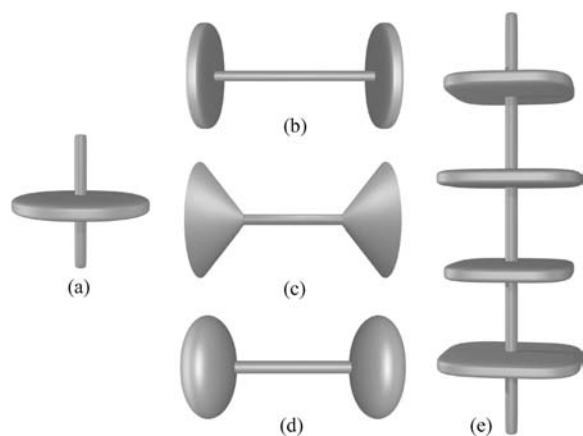


Fig. 2. Typical geometries of the wheel-and-axle host family: (a) humming-top, (b,c,d) wheel-and-axle and (e) ladder-and-platform architectures.

platform (shish-kebab, multi-decker) architecture comprises planar or bulky fragments threaded on a rod (Fig. 2e). The resulting molecule may be either oligomeric or polymeric, or may be composed of small molecules linked together by secondary bonding.

General features of the molecules belonging to the wheel-and-axle family are their increased conformational rigidity and some symmetry. These factors cut down the number of freedom degrees of the molecules thus preventing their close packing and facilitating the formation of cavity space in the crystal. It should be noted that all the molecules possess some void space near the rod. Very often this voids combine into cavities in the crystal although the relation between cavity space in the crystal and the void space belonging to a single molecule is not always evident. The following sections describe examples and variations of the basic types schematically illustrated in Fig. 2.

Platforms and humming-top geometries

Platforms and simple geometries of this section serve as building elements in the design of

more complex architectures (see further parts). The platforms may be subdivided into four most frequent types: a metal center coordinated by four terminal ligands (in Werner complexes), metal center chelated by two bidentate (or one tetradentate) ligands, the combination of two metal centers and four carboxylates and a metal center confined in a macrocycle.

Werner complexes

Numerous complexes of general formula $[MX_2A_4]$ form inclusion compounds known as “Werner clathrates.”^{24–26} In the formula, M is usually referred to a M(II) cation, X stands for a (1-) anionic ligand and A, a neutral ligand, belongs to amines such as pyridines²⁴ or α -arylalkylamines.²⁵ The inclusion in Werner complexes has been studied since 1950s when its high selectivity was reported^{24,25,27} and the use of the complexes for the separation of organic compounds was suggested.²⁷

One of the simplest Werner complexes, $[\text{Ni}(\text{NCS})_2\text{Py}_4]$ (Py = pyridine),²⁸ is shown in Fig. 3. Four pyridine ligands in the equatorial plane of the complex form a platform, while two axially coordinated isothiocyanate groups form a rod. The space around the rod and adjacent to the

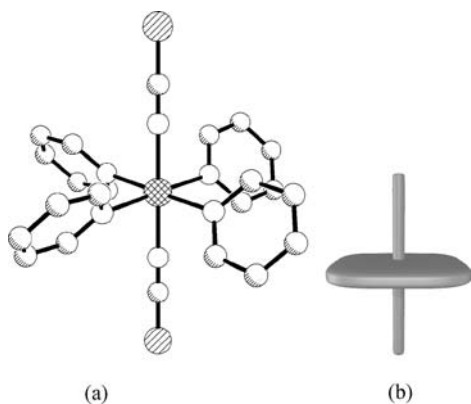


Fig. 3. Molecular structure (H-atoms are not shown) (a) and schematic representation of the molecular shape (b) of the $[\text{Ni}(\text{NCS})_2\text{Py}_4]$ complex.²⁸



Fig. 4. Schematic representation of crystal packing in the $[\text{Ni}(\text{NCS})_2\text{Py}_4] \cdot 2\text{Py}$ clathrate. Guest species are shown as white ellipsoids.²⁸

platform is not large enough to accommodate a guest molecule. However, several host molecules may form a cavity of molecular size. In the crystal structure of $[\text{Ni}(\text{NCS})_2\text{Py}_4] \cdot 2\text{Py}$, four host molecules occupy four corners of a rectangular parallelepiped to form a cage suitable for a guest molecule (Fig. 4). This type of structure is very common for Werner complexes with unsubstituted pyridine; it was observed in $[\text{M}(\text{NO}_3)_2\text{Py}_4] \cdot 2\text{Py}$ (M = Mg,²⁹ Mn, Co, Ni, Cu, Zn, Cd, Hg),³⁰ $[\text{M}(\text{NCO})_2\text{Py}_4] \cdot 2\text{Py}$ (M = Mn, Fe, Co, Ni, Cu, Zn, Cd),^{31,32} $[\text{M}(\text{N}_3)_2\text{Py}_4] \cdot 2\text{Py}$ (M = Co, Ni),³³ $[\text{M}(\text{ClO}_4)_2\text{Py}_4] \cdot 2\text{Py}$ (M = Mg, Ni),²⁹ $[\text{CuCl}_2\text{Py}_4] \cdot 2\text{Py}$,³⁴ $[\text{CrBr}_2\text{Py}_4] \cdot 2\text{Py}$,³⁵ $[\text{Mg}(\text{BH}_4)_2\text{Py}_4] \cdot 2\text{Py}$,³⁶ $[\text{Cu}(\text{NO}_3)_2\text{Py}_4] \cdot 2\text{G}$ (G = benzene, tetrahydrofuran, pyridine, chloroform),³⁷ $[\text{Ru}(\text{CN})_2\text{Py}_4] \cdot 2(\text{CH}_3\text{CN})$,³⁸ $[\text{Ru}(\text{NCS})_2\text{Py}_4] \cdot 2(\text{CH}_2\text{Cl}_2)$,³⁹ $[\text{Cr}(\text{BH}_4)_2\text{Py}_4] \cdot 2(\text{tetrahydrofuran})$,⁴⁰ $[\text{Ti}^{\text{III}}\text{I}_2\text{Py}_4]^+(\text{I}_3)^{-}$ ⁴¹ and other clathrates.⁴² Previously many of these compounds were believed to comprise hexapyridine complex cations $[\text{MPy}_6]^{n+}$ but the

supramolecular structure with two chemically nonbonded pyridines appears to be more favorable.^{42–44}

The introduction of substituents into the A ligand, especially in position 4, enlarges the effective size of the platform and intensifies the clathration ability of $[MX_2A_4]$ complexes. The complex $[Ni(NCS)_2(4-MePy)_4]$ (4-MePy = 4-methylpyridine) entraps almost any solvent upon crystallization or contact and produces clathrates of several structural types.⁴⁵ One of the polymorphs has a 3D system of pores⁴⁵ and behaves as a universal microporous sorbent.⁴⁶ Physico-chemical behavior of this complex and its Co(II) counterpart inspired the idea of “organic zeolites”, organically-based materials mimicking the remarkable properties of zeolites.⁶

The $[MX_2A_4]$ complexes can be extensively modified by the introduction of various M, X and A.²⁴ For example, the clathrates of complexes with ~ 100 different A were reported,²⁴ including 4-methyl-,^{45,47} 4-ethyl-,^{48,49} 4-vinyl-,⁵⁰ 4-phenyl-,⁵¹ 4-acetyl-,⁴⁹ 4-(N-tert-butyl-N-oxyamino)-,⁵² 3-methyl-,^{53,54} and 3,5-dimethylpyridines,⁵³ quinoline⁵⁵ and furopyridines.^{56,57} The modifications may alter the clathrate structure and selectivity towards certain guests but do not destroy the clathratogenic function of the complex molecule as long as its general humming-top shape is preserved. Also, only trans-configured complexes which display this shape were found to form clathrates, the fact clearly indicating the humming-top geometry as a decisive factor responsible for the clathration ability of the $[MX_2A_4]$ complexes.

Modified metal dibenzoylmethanates and other chelates

Planar metal bis-chelate is a convenient element in the design of humming-top molecular geometries. The axial coordination sites allow for additional coordination of two ligands above and below the equatorial plane of the complex thus producing the desired shape. Modified metal

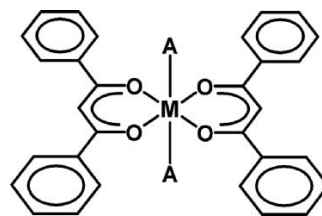


Fig. 5. Modified metal DBM.

dibenzoylmethanates (DBMs) were deliberately created as a new host entity taking into account the above considerations (Fig. 5).^{58–63} A number of metal(II) cations (M) and pyridines (A) were used to produce dozens of the $[M(DBM)_2A_2]$ complexes acting as hosts.

The equatorial part of the $[M(DBM)_2A_2]$ complex is rather flat. In spite of the rotational freedom of the phenyl rings, they tend to be close to a coplanar rather than a perpendicular position to the equatorial plane, apparently due to some interaction with pseudo-aromatic rings of the bis-chelate fragment. The coordination of an axial ligand (A) forms four shallow pockets between the ligand and the equatorial part of the molecule. In the crystal, some of these pockets are occupied by phenyl or pyridyl fragments of adjacent complexes. However, some pockets cannot be filled in this way and become available for guest species (Fig. 6a). In most cases the number of the vacant pockets on each complex is two and the resulting host to guest stoichiometry is 1:2. In the studied crystal structures the pockets combine to produce cages, channels or interlayer spaces.

The rigidity of the molecular geometry is essential. The presence of fragments that can compete with guest species for the vacant pockets either weakens or destroys the clathration ability of the complex. This possibility known as “self-inclusion” is illustrated in Fig. 6b,c. In the complex shown in Fig. 6b bulky naphthyl fragments efficiently fill two pockets after rotating perpendicular to the equatorial plane.⁶³ In the complex shown in Fig. 6c the pockets are filled with benzyl fragments attached to the chelate fragments of the complex.⁶⁴ Similar situation was observed

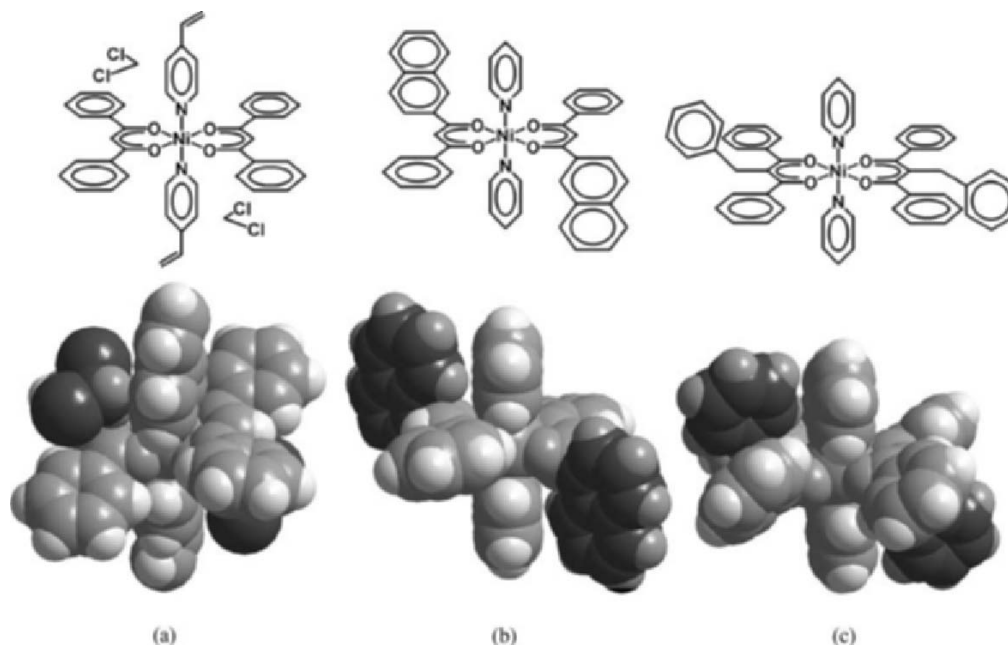


Fig. 6. Filling the pockets of host complexes with guest molecules in $[\text{Ni}(\text{DBM})_2(4\text{-Vinylpyridine})_2]^* 2(\text{CH}_2\text{Cl}_2)$ ⁶⁰ (a), with naphthyl fragments in $[\text{Ni}(\text{NBM})_2\text{Py}_2]$ ⁶³ (b) and with benzyl fragments in $[\text{Ni}(2\text{-benzyl-DBM})_2\text{Py}_2]$.⁶⁴ Space-filling models outline van der Waals dimensions; the included guests and fragments are drawn darker for clarity.

in $[\text{Ni}((i\text{-Butyl})_2\text{PS}_2)_2(4\text{-NH}_2\text{Py})_2]$ complex: the bulky iso-butyl substituents are not fixed in the equatorial plane but instead they direct toward the axial 4-aminopyridine ligand, the complex packing in a dense, solvent-free form.^{65,66} In another recently reported complex, a bulky axial ligand itself fills out the pocket and the complex forms a solvent-free crystal.⁶⁷ Another factor affecting the geometry of the $[\text{M}(\text{DBM})_2\text{A}_2]$ molecule is the nature of metal center. The replacement of Ni(II) with Zn(II) and Cd(II) in the trans-configured complexes led to cis-complexes devoid of the clathratogenic function.^{58,61}

Clathrates of $[\text{ML}_2\text{A}_2]$ complexes based on a planar bis-chelate ML_2 platform have been reported with benzoylacetonate,⁶⁸ hexafluoroacetylacetonate,⁶⁹ 2-formylphenolate,⁷⁰ 2-acylaminopyridine,⁷¹ 4-imidazolylacetate,⁷² enaminketone,⁷³ N-pivaloylbenzamidinate,⁷⁴ carbamoylpyrazole,⁷⁵ 2-pyridyltriazole,⁷⁶ dipyridyltriazole,⁷⁷ 2-pyridyloximate,⁷⁸ 2-quinolylace-

tate,⁷⁹ oxyphenylindol,⁸⁰ 4-methylbenzoylhydrazonate⁸¹ and other bidentate L-ligands. Finally, clathrates of $[\text{MLA}_2]$ complexes with tetradentate L-ligands such as Schiff bases have been reported.^{82–85}

Dimeric metal carboxylate-bridged complexes

Complexes of this type (Fig. 7) are based on a dimeric metal carboxylate unit, one of most frequently used in crystal engineering building elements. The unit itself is very stable and, with typically used M(II) centers, electrically neutral. Two additional coordination sites out of the main core make it possible to create a humming-top shape with two ligands A. These ligands may be easily replaced in order to modify the host molecule. Interestingly, the replacement may be accomplished even within a microporous solid phase, with the pores serving as transport channels for the reactant and product.⁸⁶

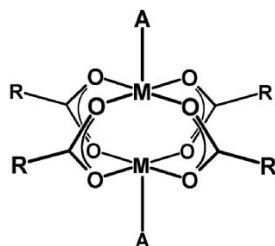


Fig. 7. Complex based on a dimeric metal carboxylate unit.

This structure was reported by Kristianson & Tergenius;⁸⁶ it comprises discrete host complexes with Cu(II) *p*-nitrobenzoate and water or alcohol molecules as additional ligands. The structure possesses channel-shape open cavity space with roughly $6 \times 8 \text{ \AA}$ cross-section of the pores. A reversible sorption was demonstrated for a series of guest molecules, from high-polar water to non-polar benzene, with the porous structure being stable to the guest exchange and removal. The authors argue that other previously reported structures^{87–89} might reveal similar sorption behavior.

Complexes of the type shown in Fig. 7 frequently form inclusion compounds. The host complexes with various metal centers were reported, including Cu(II),^{90–96} Ni(II),^{97–99} Fe(II),^{100,101} Mn(II),¹⁰² Cr(II),^{103,104} Rh(II),^{105–107} Ru(II),^{108,109} Ru(II)/Ru(III),^{109–111} Mo(II),¹¹² Re(III)¹¹³ and W(II).¹¹⁴ The complexes of Cr(II) and the following are additionally stabilized by a metal-metal chemical bond.

Complexes with porphyrins and other macrocyclic ligands

Rigid macrocyclic ligands represent a family of platforms of various composition and a great potential for modification. Some complex units formed by the coordination of deprotonated ligands to a metal cation are shown in Fig. 8. The rigidity of the units is supported by the aromaticity of the ligands. The diversification is possible through the addition of substituents on the

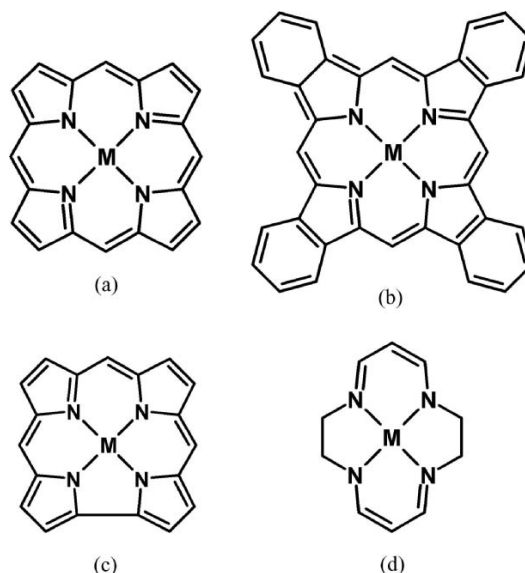


Fig. 8. Complex units comprising deprotonated macrocyclic ligands: metal(II) porphyrinate (a), metal(II) phthalocyaninate (b), metal(III) corrolate (c) and metal(II) 1,4,8,11-tetraaza(14)annulenate (d). All shown units are electrically neutral, quite rigid and planar (the annulenes may have a concave geometry).

outer rim. The planar complex units are very stable while two additional coordination sites on the metal center make it possible to attach a variety of axial ligands to create host molecules of a desired shape.

Various porphyrins form complexes which have the humming-top geometry and produce clathrates. Here only few examples will be mentioned for illustrative purposes. All three complexes of Fe(II) tetramesitylporphyrinate (out of seven), with 4-methyl-, 3- and 4-cyano-pyridines, whose crystal structures were studied had guest solvent molecules included.¹¹⁵ Four complexes of a nickel(II) porphyrinate containing twelve substituents (including ethyl- and nitro-groups) and azole-type axial ligands were isolated in form of crystalline clathrates.¹¹⁶ Although only one structure comprised complexes not interacting with each other by H-bonds, some factors such as the presence of guest molecules in all four crystals with a similar host to guest stoichiometry

indicate the molecular geometry as a main contributor to the clathration affinity of the complexes. In a series of substituted Fe(III) porphyrinates (including one phthalocyaninate) with imidazole and pyridine axial ligands, one to four moles of guest solvent were found along with anion in all eight crystal structures studied.¹¹⁷

Approximately 40% of mononuclear octahedral complexes containing phthalocyanines found in Cambridge Structural Database¹¹⁸ contain solvent molecules in the crystal structure. Some of the guest-free complexes exhibit self-inclusion (see discussion in the previous subsection) and many of them have monoatomic axial ligands and, therefore, their humming-top geometry is incomplete. Corroles¹¹⁹ is a new class of ligands related to porphyrins; examples of clathrates based on humming-top metal(III) corrolates are already available.^{120–122} Finally, clathrates of octahedral complexes based on tetraazaannulenes^{123–126} and their non-aromatic analogs (e.g. cyclams)^{127–130} are known.

Wheel-and-axle geometries

Toda's host molecules

In 1968 Toda and Akagi reported¹³¹ on host properties of tetraphenylidiols **2** and **3** (Fig. 9). These molecules formed crystalline clathrates with various organic guests: ketones, aldehydes, esters, ethers, amides, amines, nitriles, sulphoxides and sulphides. Diols of this type have become a subject of extensive studies and proved to be versatile hosts.^{132–134} However, the capability of **1–3** to form hydrogen bonds made the role of the host molecular shape ambiguous. The comparison of clathration affinity of hydrocarbons **4–6** and diols **1–3** (Fig. 9) proved that the remarkable clathratogenic properties are inherent in the both types and so the wheel-and-axle molecular geometry is a decisive factor.^{18b, 135} In particular, clathrates **1***0.5(p-Xylene) and **4***0.5(p-Xylene) were found to be isostructural.¹³⁵ A series of diols similar to **1–3** with 9-fluorenyls instead of biphenylmethy-

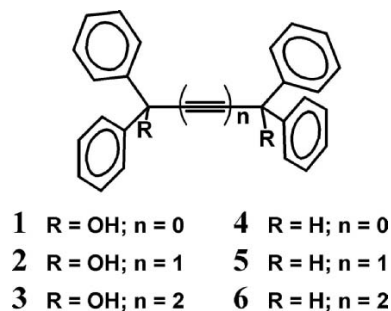


Fig. 9. Toda's host molecules.

lene fragments was also utilized extensively as host molecules.^{136, 137}

Hart and coworkers¹³⁸ studied a series of similar host molecules with triaryl ends and were able to isolate at least one clathrate (and up to five) for each host. In particular, $\text{Ar}_3\text{CC}\equiv\text{C}-\text{C}\equiv\text{CCAr}_3$ host molecules with all four Ar_3 combinations of phenyl and *p*-biphenyl enclathrated guest chloroform or aromatics. Similar structure and clathratogenic properties were reported for bis-triphenylsilane oxide, $\text{Ph}_3\text{Si}-\text{O}-\text{SiPh}_3$ (the Si–O–Si fragment is linear).^{139, 140} It is interesting to note that all these molecules combine two connected trifoil moieties (cf. Fig. 1b).

Further developments on organic molecules

The modification of the ends was performed in several ways of which one has to be mentioned. The shape of Toda's and Hart's molecules may be roughly approximated as two cones connected by a rod (Fig. 2c). The introduction of adamantyl ends resulted in so-called dumb-bell-shaped hosts (cf. Fig. 2d).¹⁴¹ Other bulky groups used successfully for this type of modification included camphor,¹⁴² borneol, fenchol,¹⁴³ triptycyl (Fig. 1c),^{15, 138} an organometallic group containing cobalt¹⁴⁴ and a galactopyranose derivative.¹⁴⁵ With only few such attempts known, the strategy appears to be very useful and connecting bigger sphere-like molecules like fullerenes¹⁴⁶ could produce novel host entities.

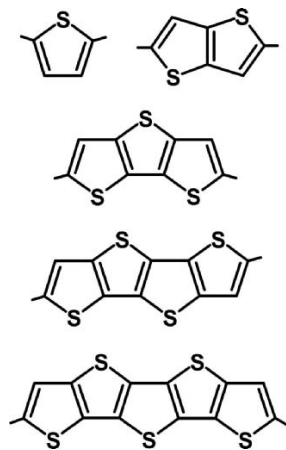


Fig. 10. Thiophene groups used as spacers in the design of wheel-and-axle host molecules.^{152, 153}

The modification of the axle proved to be fruitful as well. In order to connect two triphenylmethyl ends, Sengupta and coworkers¹⁴⁷ used spacers composed of acetylene and phenylene fragments, while Guo and coauthors^{148, 149} used hydroquinone substituted in positions 2 and 6. Weber and coworkers introduced biphenylene spacers.^{150, 151} Hurt and coworkers¹³⁸ used a number of hydrocarbon, N- and O-containing groups to connect the ends and demonstrated that the non-linear and flexible spacers support well the desired wheel-and-axle geometry and its clathratogenic function. Kobayashi's group incorporated a series of condensed polythiophenes (Fig. 10) in the host molecule and found that the host:guest stoichiometry in the resulting clathrates is related to the number (odd or even) of the thiophene rings in the spacer.^{152, 153} Ng and Hart¹⁵⁴ used N,N'-substituted ureas, diamides, diamines and related molecules imitating the wheel-and-axle geometry and with 24 host compounds, out of 38 tested, were able to isolate clathrates. A wide range of guest solvents was utilized and the selectivity of inclusion was demonstrated.

Assembled host associates

A suitable host geometry may be accomplished not only in a single molecule but in an

associate of two or more molecules linked to each other with non-covalent bonds. In many cases the geometry of such associates may be predicted and planned, and the self-assembly of the new host entities occurs simultaneously with the formation of inclusion compounds. Some examples of such associates are shown in Fig. 11.

The complex of triphenylsilylacetylene and triphenylphosphineoxide (Fig. 11a) was isolated as a solvent-free crystalline solid but the presence of four crystallographically independent associates in the unit cell indicate packing problems and imply the potential of the complex to act as a host.¹⁵⁵ The dimer of 4-tritylbenzoic acid (Fig. 11b) persistently forms in the solid phase and acts as a versatile host.^{156, 157} Tris(benzo[*b*]thienyl)methanol is a trifol-type host molecule with a hydroxy-group; in one of its clathrates with acetonitrile, a supramolecular associate (Fig. 11c) was observed where the acetonitrile molecule functions as both the connector and a guest.¹⁵⁸ Finally, two molecules of triphenylphosphineoxide assembly with two molecules of water to form a host associate (Fig. 11d) observed in the inclusion compound of the host with tetrachloropyrocatechin.¹⁵⁹

Metal-organic molecules

The use of metal centers and coordination bonds opens new opportunities in the design of wheel-and-axle host molecules. The metal centers make it possible to create a wider set of geometries than carbon, such as square-planar and octahedral geometries. The coordination bonds are thermodynamically as strong as covalent bonds but kinetically they are more labile; therefore, metal-organic molecules may be easier synthesized, modified, and repeatedly assembled and disassembled under controlled conditions. In addition, the presence of coordination sites makes it possible to incorporate further functionalities in the porous materials to create catalysts, ion exchangers and so on.

Two types of wheel-and-axle metal-organic molecules may be distinguished. In the first type,

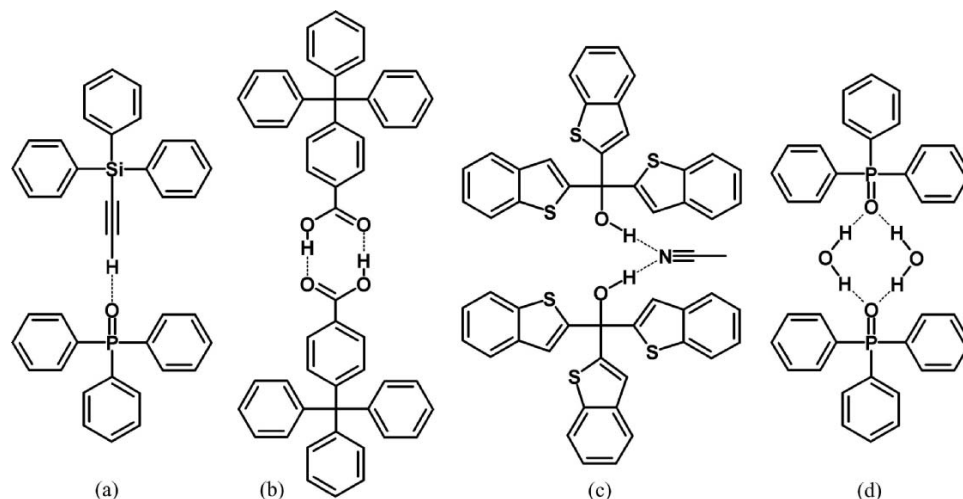


Fig. 11. Hydrogen bonding associates imitating wheel-and-axle host molecules: two complementary molecules (a),¹⁵⁵ two identical self-complementary molecules (b),^{156,157} two molecules connected through a third molecule (c),¹⁵⁸ two molecules connected through two other (water) molecules (d).¹⁵⁹

a metal center is incorporated in the end groups. The end group may be a bulky complex or platform (such as shown in Fig. 8); a vacant coordination site is used for connecting two end groups through a bridging ditopic ligand (spacer). In the second type, metal centers is an essential part of the spacer, with their trans-directed coordination sites used to connect end groups.

One complex of the first type comprises two bis(2,2'-bipyridyl)copper(II) units connected by carbonate, the Cu(II) atom coordinated by five atoms, four N and one O.¹⁶⁰ The Cu...Cu separation is 5.3 Å; the host molecule void space (between the two end groups) is partially filled with end groups of adjacent complexes and partially with hexafluorophosphate anions. The residual cavities arising in the crystal packing are filled with guest dimethylformamide species. Other reported cationic host species comprised bulky end groups containing Ni(II),¹⁶¹ Cu(II)¹⁶² and connected by aromatic dicarboxylate ligands, with anions and neutral organic molecules acting as guests. A similar neutral complex with Ru(II)/Ru(III) was reported as a clathrate with benzene.¹⁶³ One cationic¹⁶⁴ and one neutral¹⁶⁵ host species had oxalate ligand as a spacer, while the end groups were represented by Zn(II) cyclam

(tetraazacyclotetradecane) platforms and Fe(III) bis(acetylacetonate) units, respectively. Interestingly, the latter host complex was isolated in both solvated and guest-free crystalline forms which displayed basically the same structure but the insertion of the guest 1,2-dichloroethane resulted in >25% expansion of the crystal in one dimension.¹⁶⁵ Two cationic host species with Pt(II) and bipyridyl ligands were reported as clathrates containing, along with counter-anions, methylene chloride/water and acetone.¹⁶⁶ Two neutral complexes with bulky end groups containing Rh(III) and Co(III)/Rh(III) and connected by flexible spacers (S,S'- and N,S'-ligands, respectively; metal...metal separation ~ 8 Å) were reported as clathrates with chloroform and acetone.¹⁶⁷ A series of cationic and neutral Ru(II) organometallic compounds containing Ru-C≡C-C≡C-Ru and Ru=C=C-C=C-Ru cores, respectively, were reported to form clathrates with acetone, methylene chloride and hexane.¹⁶⁸ Finally, one more complex of this kind displayed a separation of >20 Å between metal centers in the fragment Ru-(C≡C)₇-Ru and contained seven moles of guest benzene.¹⁶⁹

Goldberg and coauthors used a series of nine rigid and flexible bidentate ligands to

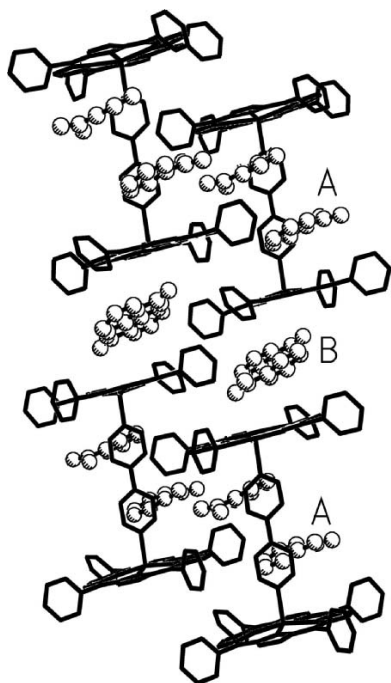


Fig. 12. A fragment of crystal packing in $[\text{Zn}_2(\text{TPP})_2(\text{bipy})]^+4(\text{nitrobenzene})$ (TPP is tetraphenylporphyrin; bipy is 4,4'-bipyridyl).¹⁷⁰ Guest molecules are outlined in sticks-and-balls. Note that the host intramolecular spaces are partially filled with platforms of adjacent host molecules and with guest molecules of type A. Guest molecules of type B reside in cavities located outside the host molecules.

connect metal(II) (Mn, Co, Zn) tetraarylporphyrinate platforms.^{170,171} The resulting dimeric complexes displayed metal . . . metal separation from 8–20 Å and all produced inclusion compounds with organic solvents (11 structures with nitrobenzene and chloroform as guests were reported). A common feature of these structures is a parallel alignment and interdigitation of the host molecules. Guest species accommodate the residual voids of the crystal lattice; the voids may be composed of intramolecular spaces between the platforms or may not (Fig. 12). Similar work was reported by Litvinov and coworkers.¹⁷² An example of analogous host complex with phthalocyaninate platforms is also available.¹⁷³

Some complexes of the second type are shown in Fig. 13. All these molecules or ions were found to act as host species in inclu-

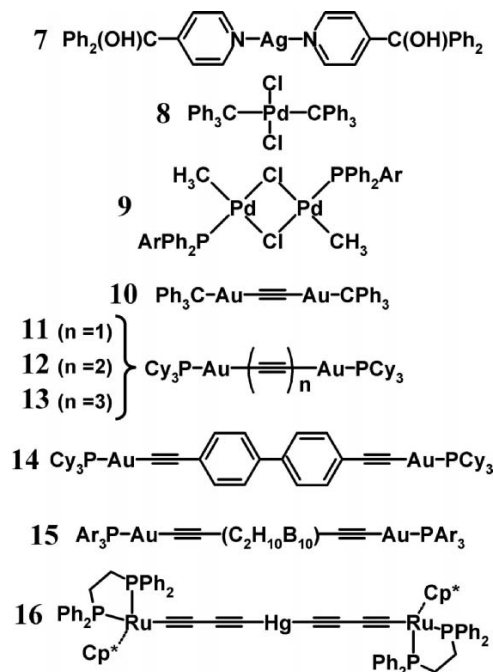


Fig. 13. Wheel-and-axle host molecules with metal centers incorporated into the spacer (Ph = phenyl; Ar = aryl; Cy = cyclohexyl; $\text{C}_2\text{H}_{10}\text{B}_{10}$ = 1,12-dicarbadodecaborane(10); Cp^* = pentamethylcyclopentadienyl).

sion compounds with various organic guest solvents. The cation **7**¹⁷⁴ is based on Ag(I) center with approximately linear coordination of two N-containing ligands with bulky ends. Neutral complex **8**¹⁷⁵ is an example of host molecules based on square-planar coordination geometry of Pd(II). Two trans-situated chloride anionic ligands leave the other two trans-positioned coordination sites to bulky organic groups acting as ends. Other reported host complexes of this type were based on PdCl_2 ,^{176–180} $\text{Pd}(\text{CH}_3)\text{Cl}$, $\text{Pd}(\text{CH}_3\text{COO})_2$,¹⁸⁰ PdI_2 ,¹⁸¹ $\text{Pd}(\text{CN})_2$,¹⁸² PtCl_2 ,¹⁸³ PtHBr ,¹⁸⁴ and other trans-“junctions”. One of Pd(II) complexes was reported to form a clathrate with seven guest chloroform molecules per one host unit.¹⁸⁵ Complex **9** exemplifies another way of creating the wheel-and-axle geometry, with two Pd(II) centers linked by two bridging chlorides.¹⁸⁶ Complexes **10–15** illustrate the use of Au(I) linear connector for building and lengthening the rods, with the separation between the junction atoms

of the end trityl groups varying from 10 to 21 Å. The complex **10** was isolated as 1:2 (host:guest) clathrate with benzene, while its analog with 3-methylphenyls was obtained both as 1:1 clathrate with benzene and as a guest-free form. Remarkably, all three crystals were isomorphous indicating that the host matrix retains both after the removal of guest and after the modification of the host molecule.¹⁸⁷ The complexes **11**, **12**,¹⁸⁸ **13**,¹⁸⁹ **14**¹⁹⁰ and **15**¹⁹¹ demonstrate the lengthening strategy through the introduction of additional rigid fragments into the central bridging ligand. Complex **16**¹⁹² illustrates the use of Hg(II) cation; the complex has metal centers not only within the spacer but also within the end groups and may be assigned to both types.

Ladder-and-platform geometries

Increasing dimensionality of host species in soft materials

Clathratogenic potential of a host component and stability of the host framework can be enhanced by increasing the dimensionality of the host molecules. Restricting freedom of the host units by connecting them together disfavours the attainment of dense structures and increases the probability of porous architectures. Stability of the porous architectures may increase either on thermodynamic or kinetic reasons, due to non-existence of more stable dense form or due to a significant kinetic barrier for the collapse of the porous structure which would require the break of some chemical bonds. At the same time, in order to keep the remarkable properties of soft materials, it is important to keep van der Waals and other weak interactions dominating in some directions in the solid phase.^{1–3} Therefore, oligomeric and low-dimensional polymeric molecules seem to be optimum.

Oligomeric and polymeric structures

Successive construction of monomeric, oligomeric and polymeric host molecules is

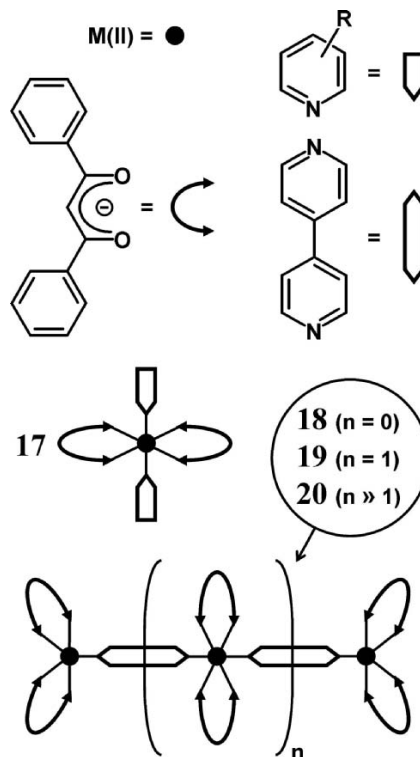


Fig. 14. Assembly of monomeric (**17**), oligomeric (**18**,**19**) and polymeric (**20**) host molecules from metal dibenzoylmethanates and pyridyl-type ligands.¹⁹³

illustrated in Fig. 14.¹⁹³ The coordination of two dibenzoylmethanate (DBM) units and two pyridines to a metal center produces a humming-top geometry **17** and the molecules of this type were described in the section *Modified metal dibenzoylmethanates and other chelates*. Connecting two dibenzoylmethanate units with 4,4'-bipyridyl produces a dimeric complex with wheel-and-axle geometry **18**, with the metal atoms five-¹⁹³ or six-coordinated¹⁹⁴ (the latter situation requires additional terminal ligands). The trimeric complex **19** has one middle platform and two bulky end groups separated by rigid 4,4'-bipyridyl spacers. Such a complex was isolated as a clathrate with dimethylsulfoxide with 1:5 host to guest ratio.¹⁹³ The guest dimethylsulfoxide molecules were found in the intramolecular spaces that were also partially occupied with end groups of adjacent trimers aligned parallel

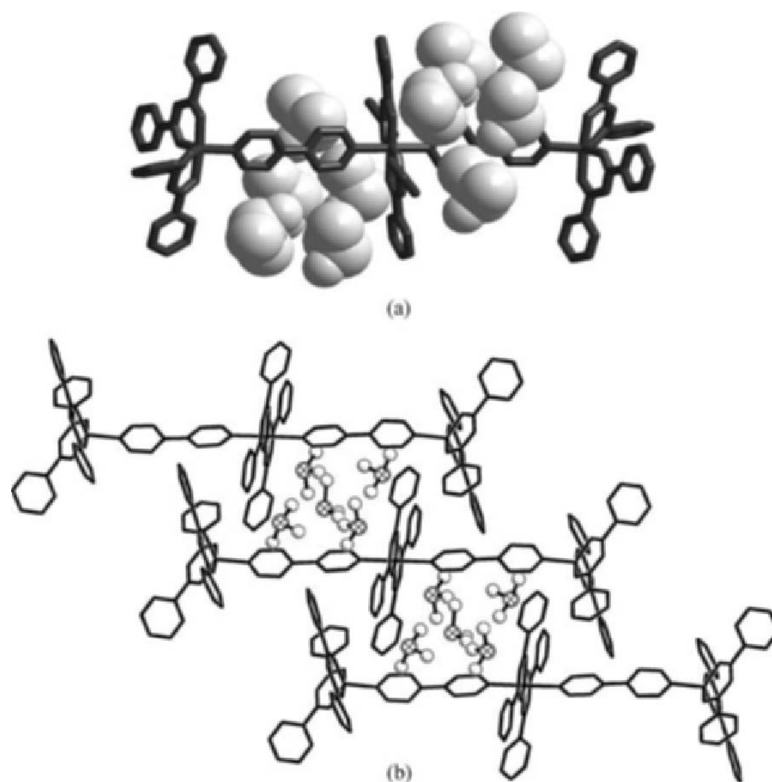


Fig. 15. Crystal structure of $[\text{Zn}_3(\text{DBM})_6(\text{bipy})_2] \cdot 5(\text{dimethylsulfoxide})$.¹⁹³ The location of guest molecules in the intramolecular spaces of the host trimer (a) and a fragment of crystal packing showing interdigitating host trimers (b).

(Fig. 15). Further expansion leads to a polymeric complex **20**^{193,195} with a geometry known as “ladder-and-platform,” “shish-kebab,” or “multi-decker” architecture.

Synthetic approaches to the step-by-step assembly of ladder-and-platform molecules were reported and discussed.^{193,196–201} In some cases a desired oligomer may be prepared using certain ratios of reagents and the template effect of a guest solvent. In other cases the product is a mixture of oligomers. There still have been very few communications where the isolation and clathration ability of more than two host molecules differing in the degree of polymerization were described.^{193,198}

Examples of reported trimeric host molecules include a complex with three Zn(II) tetraphenylporphyrinate platforms connected

with 4,4'-bipyridyl spacers,¹⁹⁸ complex with three Mn(III) tetraphenylporphyrinate platforms connected with bridging formate anions,²⁰² complex cations with Mo(V) tetraphenylporphyrinate platforms linked with oxo-anions²⁰³ and with Cu(II) cyclam platforms linked with bridging chlorides.²⁰⁴ One more trimeric host complex contains a central Si(IV) phthalocyaninate unit connected with two Zn(II) porphyrinate platforms through 4-pyridinolates bridges.²⁰⁵ Trimeric^{206–208} and tetrameric^{207–209} cationic complexes were reported with oxo-anions acting as linkers and platforms based either on complexes of tetradentate Schiff bases with rhenium,²⁰⁶ titanium,²⁰⁷ vanadium²⁰⁹ metal cations or on terpyridine-uranium(IV) units.²⁰⁸ Complexes with a central platform and bulky end groups, similar to **19** (Figs. 14 and 15),¹⁹³ were

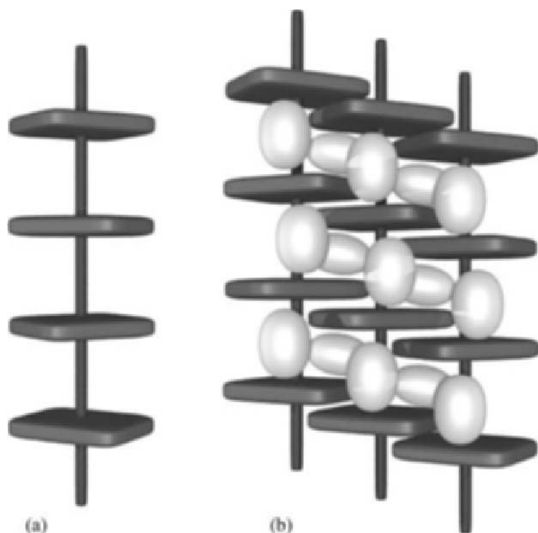


Fig. 16. Schematic representations of coordination polymer **20** (see Fig. 14) (a) and crystal packing in $[M(\text{DBM})_2(\text{bipy})]_n \cdot 2(\text{chlorobenzene})$ ($M = \text{Zn}, \text{Ni}$).¹⁹⁵ Guest molecules are drawn as white ellipsoids.

reported with a central porphyrinate platform and bulky Cu(II) complex units²¹⁰ and with a cyclam platform (similar to shown in Fig. 8d) and end triphenylborate groups,²¹¹ with cyanides acting as linkers in both complexes. Finally, a complex with di-rhodium tetracarboxylate central unit and organoruthenium end groups²¹² and a cationic host complex with tetrapyridine central platform (similar to shown in Fig. 3a) and end bulky ruthenium complexes attached through cyanides²¹³ were reported.

Typical crystal packing of polymeric host molecules is shown schematically in Fig. 16.¹⁹⁵ The molecules align parallel and interdigitate. This mode of packing leaves a significant amount of cavity space in the structure available for guest molecules. The complex $[\text{Ni}(\text{DBM})_2(\text{bipy})]_n$ behaves as a universal sorbent material absorbing gases and organic solvents. The inclusion of some guests follows Type I isotherm and occurs practically without a host structure change indicating the presence of permanently available micropores in the material which thus can be classified as organic zeolite. The inclusion of other guests causes structural reorganization; eight new

crystal structures were observed with 11 tested guest solvents. Presumably, the main features such as the parallel alignment and interdigitation of the host molecules are retained in all these structures, but slight packing and conformational changes take place and they are individual nearly for every new guest. The changes are visible due to a noticeable color change accompanying the inclusion process.¹⁹⁵ A reversible sorption without changing the porous crystalline form was reported for another polymer with bis-chelate platforms. The crystal structure of an inclusion compound of the polymer $[\text{Ni}(\text{butylxanthate})_2(\text{bipy})]_n \cdot 2n(\text{CCl}_4)$ reveals a similar parallel alignment of the host polymeric chains and channels stretching approximately perpendicular to the chain direction.²¹⁴

The inclusion ability of ladder-and-platform polymers depends on the size of the platform. Coordination polymers with smaller platforms based on acetylacetonate,^{215,216} hexafluoroacetylacetonate²¹⁷ and picrate²¹⁸ connected with 4,4'-bipyridyl reveal a typical parallel arrangement of polymeric molecules but form guest-free crystals. In contrast, those with bigger platforms, based upon thenoyltrifluoroacetate^{219,220} and aforementioned dibenzoylmethanate,^{193–195} entrap up to two moles of guest.

Another group of coordination polymers comprises complexes with macrocyclic ligands. Cyclam platforms bridged by hydrogen sulfide and chloride anions were utilized in a series of clathrates comprising both counter-anions and neutral guest molecules included in the crystal lattice.²²¹ Neutral polymeric molecules with porphyrinate platforms connected with diammine^{170,222} and dicyano ligands^{223,224} were found to entrap guest solvents. At least one polymeric host with phthalocyaninate platforms was reported.²²⁵

A fair number of electrically neutral ladder-and-platform-type polymers with “shish-kebab” shape were constructed using the dimeric metal carboxylate unit (cf. Fig. 7). The units were based on Cu(II),^{226–233} Mo(II),^{234,235} Ru(II)/Ru(III)^{236,237} and Rh(II)^{238–244} methyl-

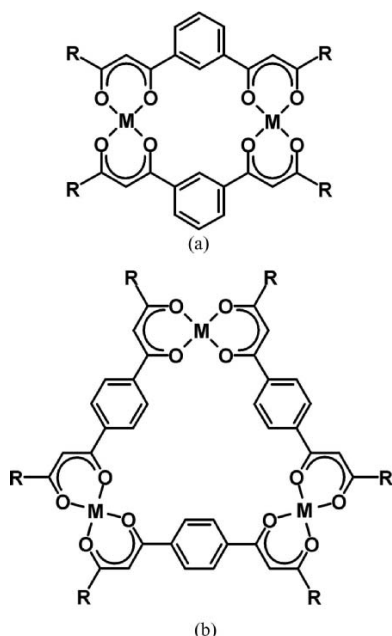


Fig. 17. Binuclear (a) and trinuclear (b) platforms formed by the assembly of metal cations M with two isomers of bis(β-diketonate)phenylene acting as ditopic ligands.

,^{228–231, 235, 237, 239} trifluoromethyl-,^{234, 238, 240} phenyl-^{227, 232, 233, 236, 241–244} and pentafluorophenyl-carboxylates.²²⁶ Bipyridyl-type ligands,^{229–233, 235, 243} pyrazine,^{227, 232, 241, 242, 244} 1,4-dioxane²²⁶ and other bidentate ligands were used as spacers. Some of these polymers displayed a zig-zag structure, with the platforms being not parallel to each other.^{228, 229, 233, 240} Various organic solvents and some gases (CO₂,^{232, 242} N₂O,²⁴¹ O₂²⁴⁴) were included as guest molecules in these solids.

Takamizawa and coworkers²⁴⁵ studied the properties of 1D complex [Rh^{II}₂ (phenylcarboxylate)₄(pyrazine)]_n and found that the crystalline polymer reveals a dense packing without solvent molecules included or cavity space available. Nevertheless, the material behaves as a microporous sorbent with Type I sorption isotherm and the micropore volume of 0.16 cm³/g (sorption of N₂). Presumably, a very low gate pressure of the guest induces a structural change in the material that makes it microporous.

Finally, supramolecular 1D polymers were reported formed as chains of H-bonded humming-top molecules [M(DBM)₂(isonicotinamide)₂] (M = Co(II), Ni(II)).²⁴⁶ The new hosts produced clathrates with a range of guest solvents.

Binuclear and polynuclear platforms

The increase of the pore size, capacity and stability of porous architectures based upon ladder-and-platform molecular geometries may be achieved through the increasing size and nuclearity of the platform. Examples of such platforms are shown in Fig. 17. The assembly of two metal(II) cations M and two 1,3-bis(β-diketonate)phenylene ligands (each bearing the charge of 2-) produces a neutral binuclear complex with a flat shape (Fig. 17a).²⁴⁷ This unit may be incorporated in a further geometry due to apical coordination sites on the metal cations (Fig. 18). The combination of the platform (Fig. 18c), terminal (Fig. 18a) and bridging (Fig. 18b) ligands may produce a double humming-top molecule (Fig. 18d), staircase-type 1D polymer (Fig. 18e) or double-strand 1D polymer with ladder-and-platform architecture (Fig. 18f). The latter geometry is more stable and robust than the geometry

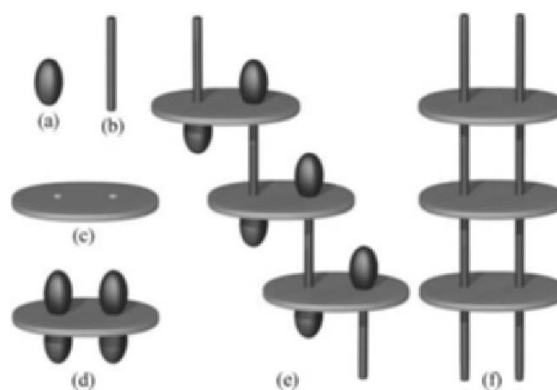


Fig. 18. Design of molecular geometries using binuclear platforms: terminal ligand (a), bridging ligand as a spacer (b), binuclear platform (c), double humming-top geometry (d), staircase geometry (e), double-strand ladder-and-platform geometry (f).

shown in Fig. 16a: the platforms are doubly linked to each other and fixed (cannot rotate). Besides, the intramolecular spaces are bigger that should increase the amount of cavity space in a potential porous material. At the same time, the resulting host materials will remain “soft” due to van der Waals type of packing of the polymeric molecules in a crystal. Another, 1,4-isomer of the ligand produces trinuclear platforms (Fig. 17b) that can be utilized in a similar way.²⁴⁸ This example illustrates how the geometry and nuclearity of platforms are programmed on molecular level in the building units utilized in their design.

Reported clathrates with double humming-top complexes (Fig. 18d) were based on tetradentate bis(β -diketonates) (up to four molecules of guest per one host complex),^{249–251} similar O,S-ligands,^{252–253} tetradentate N-ligands (cationic complexes),²⁵⁴ octadentate N-ligand (anionic complex),²⁵⁵ tridentate N,O-ligand,²⁵⁶ macrocyclic hexadentate N,O-ligand (cationic complexes with different metal centers in a single platform)^{257,258} and a combination of ligands forming the platform.^{259,260} Few reported clathrates were based on humming-top complexes with trinuclear^{248,261–264} and tetranuclear²⁶⁵ platforms. Several reported complexes comprise two binuclear platforms linked with two spacers.^{266–269} A series of three complexes with complex units based on metal clusters connected by two spacers of variable length presents another illustration of the design strategy.²⁷⁰

Both staircase (Fig. 18e)²⁵¹ and double-strand ladder-and-platform^{247,271–275} (Fig. 18f) host 1D polymers were reported. Two examples of ladder-and-platform complexes are presented in Fig. 19. In $[\text{Cd}_2(\text{saccharinate})_4\text{L}_3]_n \cdot 2n(\text{CH}_2\text{Cl}_2)$ (**21**) ($\text{L} = 1,4\text{-bis}(4\text{-pyridyl})\text{-}2,3\text{-diazabuta-}1,3\text{-diene}$),²⁷⁴ each Cd(II) cation has a trigonal bipyramidal environment of five nitrogen atoms, two from saccharinate anions and one from L in the equatorial plane and two from two L coordinated axially. Therefore, the L ligand both takes part in the formation of the platform and acts as a spacer. In $[\text{Zn}_2(1,3\text{-bis}(\beta\text{-diketonate})\text{phenylene})_2(\text{bipy})_2]_n \cdot 4n(\text{dimethyl-}$

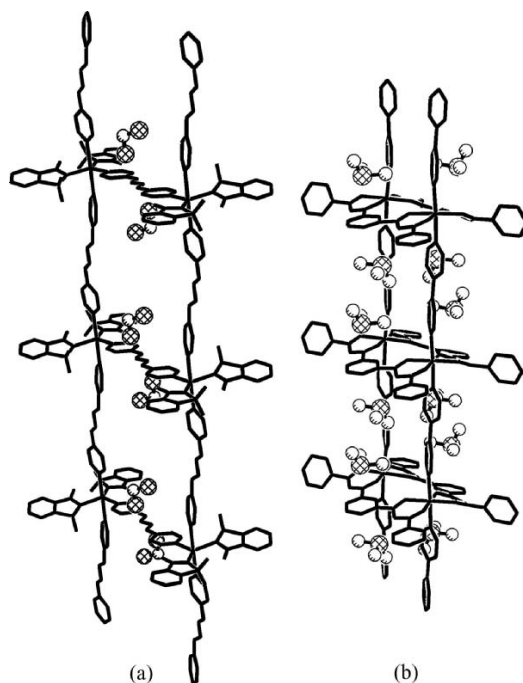


Fig. 19. Fragments of the crystal structures of **21** (a) and **22** (b). A section of double-strand host molecule and adjacent guest species are shown for each structure.

sulfoxide) (**22**),²⁴⁷ each Zn(II) cation has an octahedral coordination, of four oxygen atoms from two bis(β -diketonates) in the equatorial plane (see Fig. 17a) and two nitrogen atoms from two 4,4'-bipyridyl ligands coordinated axially. The separation between the platforms is ca. 16 and 11.5 Å in **21** and **22**, respectively. In both structures, the polymeric molecules reveal a parallel alignment and interdigitation (Fig. 20). The packing in **21** is more efficient because the polymeric chains interdigitate sharing their wider sides; (Fig. 20a) the residual cavity space between every two adjacent platforms is filled with two guest molecules. The packing in **22** is less efficient, more cavity space is available, (Fig. 20b) and four guest molecules occupy the space between every two adjacent platforms.

Very recently, a triple-strand ladder-and-platform host architecture was reported which forms a significant amount of cavity space in the crystal structure.²⁷⁶ Finally, coplanarly-linked metal porphyrinates^{197,277–279} is a useful element

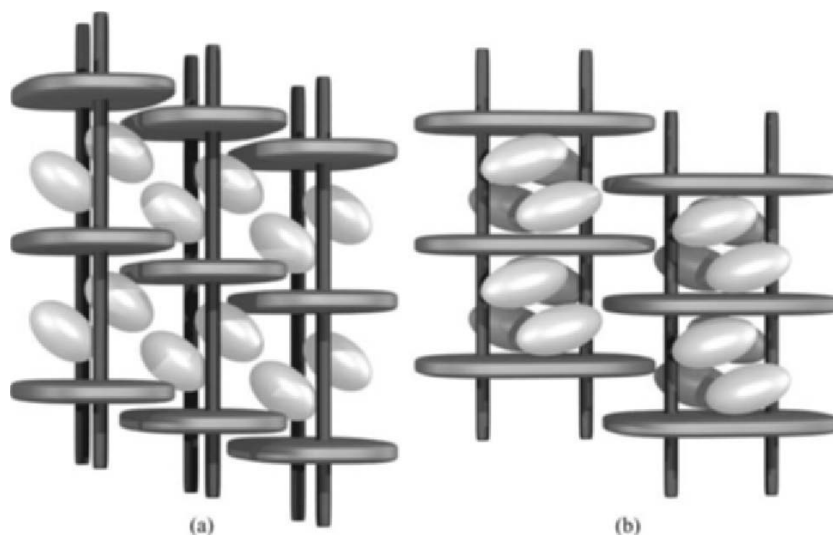


Fig. 20. Schematic representation of crystal packing in **21** (a) and **22** (b). Guest molecules are drawn as white ellipsoids

for creating polymeric ladder-and-platform geometries. The linking options vary from covalent to coordination and hydrogen bonds.

Conclusion

This review considers one type of molecular geometries that generate porosity in crystalline solids. A broader picture would require addressing to other sources illustrating such geometries and approaches.^{3,6,7,18,22,197,277,278,280–288} However, the purpose of this writing is to demonstrate the realization and use of some general principles of molecular geometry and crystal packing in the design of novel soft materials. In particular, the design of oligomeric and low-dimensional polymeric host entities seems to be a very promising strategy that is readily applied to metal-organic molecules. Apparently, this strategy may be employed not only in the design of crystalline solids but also for porous materials with no or low crystallinity. Another advantage of metal-organic hosts is the presence of metal centers that may form active sites providing materials with a desired functionality.

An important direction of future studies should be the elucidation of sorbent and other properties and functionalities in the materials. Many materials mentioned in this review were not tested for such properties and their fundamental characteristics (stability, robustness, clathratoric affinity and guest preferences, reversibility of inclusion and so on) and ability to function in practically useful processes (physical and chemical sorption, catalysis, ion or molecular exchange, chemical reactions and so on) remain unknown. Hopefully, the supramolecular approach demonstrated in this paper will be successfully combined with the knowledge and methodology of materials chemistry.

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