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Assembly of metal ions and ligands with adaptable coordinative tendencies as a route to functional metal-organic solids

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Abstract

The majority of efforts on metal-organic frameworks (MOFs) concern their rational design and, intuitively, researchers are drawn to assembly units with well-defined, reliable coordinating tendencies. Assembly units with less well-defined properties are generally less employed. This concept paper discusses the merits of using adaptable components for the assembly of functional MOFs. "Adaptable" components, whether for the metal ion or for the ligating group, are defined as those having several coordination modes within a narrow energetic range. Use of these assembly units can lead to new solids with: (i) highly dynamic properties; (ii) new inorganic structural motifs; and possibly (iii) high thermal stabilities. The article, to facilitate comparison, considers a framework on the basis of metal ion, coordinating functionality, and organic spacer. Networks with one, two and three "adaptable" units are then discussed. Ultimately, the illustration that less well-defined properties does not necessarily translate to less functional materials will be made.

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1. Introduction

In the study of metal-organic frameworks (MOFs), the ultimate goal is the formation of a functional material [1]. Presently, the most sought after applications include gas storage devices, selective separators, and molecular sensors.

Approaches to the rational design of MOFs have focused on predictable assembly, often drawing analogy to known mineral frameworks [2] or comparing to net topologies [3]. Intuitively, the likelihood of a predictable assembly will be increased by employing components with well-defined, regular bonding tendencies. Extending this train of thought, regular bonding is associated with strong, directional interactions. From this core premise has arisen the "secondary building unit approach" which has been highly successful for frameworks incorporating square and octahedral polycarboxylate metal clusters [4]. The structures are thus composed of well-defined coordination vertices linked by rigid organic spacers. These highly ordered solids display permanent porosity adjustable simply by altering the organic linkers [5].

Contrary to the above example, most well-intentioned attempts to design functional MOFs from first principles have not been so successful. Quite simply, the regularity observed in the coordinative trends of a ligand in a discrete molecular assembly do not necessarily translate to an infinite network, especially in cases where the idealized extension of the discrete structure into a network necessitates the formation of an open framework.

This brings us to the question of, "Where does network design fall short?" Essentially, an idealized design based upon linked nodes and vertices is only useful if the interactions sustaining the building unit can translate into formation of an idealized (open)

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framework. There are enthalpic requirements to fill space and, as the network forms, this strain can lead to different topologies incorporating distorted building units which then propagate a non-desired structure. Should appropriate guest molecules be included in the structure, an open framework material may result, which may or may not have the desired topology. In these cases, removal of the guests frequently results in an undesirable collapse of the network to a denser phase. "Third generation" solids, as defined by Kitagawa and Kondo [6], can regain their native form upon reintroduction of the guest molecules. This dynamic aspect to their structures offers potential in terms of switchable "smart" solids [7]. As such, they are of interest more as complements to permanently porous zeolite-like solids rather than replacements for them. Dynamic solids offer different applications than their rigid counterparts, particularly as sensors, due to their ability to reversibly adjust structure in response to external stimuli. In this respect, strong and highly directional bonding may be deleterious to structural dynamics as the energetic wells in the reaction profile should be deeper. Thus, the energy difference between the open and dense phases of an inclusion framework may be insurmountable resulting in an irreversible collapse.

The subject of this concept paper is the use of components with adaptable assembly characteristics for the formation of functional metal-organic solids. As well-defined assembling units are inherently linked to more strongly bonding entities, so should assembly units with adaptable tendencies be correlated with weaker bonding. At this point, it would be useful to indicate what is meant by "adaptable" components [8]. Typically, when the rational assembly units of these coordination networks are considered, it is with respect to the metal ion, counter ion and the ligand. For the purposes of this article, it is more meaningful to partition the components of a network as follows; the metal ion, the Lewis basic functionality of the ligand and the organic spacer unit of the polydentate ligand. With respect to the ligating functionality, carboxylate and pyridine derivatives have been widely studied owing to the regularity of their bonding. While RCOO– groups can vary their coordination, in general, a chelated form or some known cluster are the likely products especially under regimented synthetic conditions [3,9]. While a wide range of poly pyridine ligands are known, the monodentate coordination of each pyridine ring remains constant [10]. In contrast, a sulfonate group can range in its ligation from simple monodentate coordination through to a μ6-bridging mode including all modes in between [11]. Phosphonate groups, in addition to coordinating in a variety of different modes, can exist in different states of protonation [12]. Coupling the variable coordinating modes with the spherical shape of the sulfonate and phosphonate groups enables ligation in one, two, or three dimensions versus the 1-D coordination of, for example, a pyridine-type ligand. With respect to metal ions, much research has been devoted to centers with very reliable geometrical preferences (e.g. square planar palladium(II) [13]). An adaptable metal center would be one without strong geometrical preferences. For transition metals these could be ions with no LFSE such as the d^{10} ions silver(I) or zinc(II). Looking at other regions of the periodic table, even more adaptable ions are available in the lanthanides and heavier alkaline earths. These ions are usually 7–9 coordinate with a coordination sphere typically described as irregular. Gain or loss of a ligand in these centers is much more facile than in a first row transition metal. Finally, with regards to the organic linker, adaptable would simply refer to flexible spacers with high degrees of rotational freedom such as saturated alkane chains.

To this author's line of thinking, there are three advantages to the use of adaptable components in the assembly of a MOF: (1) structurally dynamic framework solids [14] should be facilitated by this approach as several structures would exist within a smaller energetic range. Benefits of these solids have been discussed above. (2) New structural motifs should be enabled by this approach and, of course, with new structures would come opportunities for new functions. In an assembly where the metal and ligating functionality are completely structure determining with respect to the geometry of the vertex, the organic moiety adopts the role more of a spacer (albeit of defined shape and size). In the case of an adaptable assembly, a rigid spacer could play a much larger structure-defining role in that it could actually dictate the structure of the metal–ligand aggregate. Control of the dimensionality of a solid is key in this light [15]. (3) The final, and perhaps least immediately evident, advantage is, the formation of robust and ordered open framework materials. Adaptable components enable the ready energetic minimization of a structure and this can lead to tremendously stable structures. While this statement may seem contradictory in light of the comments above, examples to follow will show that the stability and dynamics of a solid are not mutually exclusive. An important factor to keep in mind is that there are three components (metal ion, ligating group, and spacer) to be considered. Adaptability in even one constituent can be sufficient to impart adaptable characteristics upon the entire framework. Several excellent examples illustrate more than one of the salient features discussed above and so, examples will be discussed more in light of how many adaptable components they contain rather than which properties they demonstrate. This article will primarily focus on systems where the flexible aspect of the material stems from the metal–ligand interaction. Extending the thinking of weaker interactions, the use of non-covalent interactions to form adaptable solids is a worthy pursuit and several groups have made significant progress in this regard using both H-bonding and π stacking interactions with exclusively organic molecules [16] or with coordination assemblies [17].

2. Systems with a single adaptable component

As a starting point, assemblies with only one adaptable component will be considered. In this vein, researchers have typically employed either a flexible linker or a metal ion with a pliant coordination sphere. The first case involves the use of a flexible linker to join metal ions and ligating groups with well-defined coordinating tendencies. There are numerous examples of these systems employing ligands such as pyridines [18], carboxylates [19] or other functionalities [20], linked by some spacer unit, usually an alkane chain, which offers large degrees of conformational freedom. In general, while some of these systems can display sponge-like properties, the reversibility of this process is generally lacking relative to the examples to follow. One example that was recently reported involved a more defined flexible linker, 2,2-bi(3-hydroxy-1,4-naphthoquinone) [21]. This ligand acted as a hinge with rotation about a single bond which directed the mutual orientation of two-metal chelating sites. The availability of new structures was readily apparent as, with divalent metal cations, four families of structures were observed as indicated schematically in Fig. 1. The diversity observed was attributed both to the ability of the bhnq^{2-} ligand to twist about a range of dihedral angles as well as different coordination modes of the metals. Interestingly, for the copper(II) systems, the frameworks were able to respond to different vapors with color changes. This vapochromic behavior stemmed directly from the adaptable nature of the spacer in the ligand and the ability of the network to flex.

Another common approach to incorporating a single adaptable unit into a framework solid is the choice of the metal ion. The use of adaptable metal ions has largely not been discussed specifically as such; more frequently, structural diversity is referred to, as fairly commonly for silver(I) [22]. Heavier alkaline earth ions have largely been ignored primarily owing to their variable coordination [23]. With regards to lanthanides, incorporation into a framework is often with the goal of incorporating fluorescence [24] rather than a metal center with several coordination geometries. Another motivation is a higher coordinate node for the formation of new structural net topologies [25]. However, while adaptable structures have not been a major motivation, a significant number of the lanthanide carboxylate networks illustrate nicely the benefits of adaptability.

A number of groups used the high and variable coordination numbers of lanthanide ions to form 3-D open channel structures with polycarboxylate ligands (terephthalic acid [26], terephthalic acid and hydroxide [27], and 1,2,4,5-benzenetetracarboxylic acid [28]) where water occupied pores as well as coordinating to the metal ion. Non-coordinated and, importantly, coordinated water in these examples could be removed to give solids which retained order and could resorb guest molecules including NH_3 (Fig. 2) [26]. The ability of the

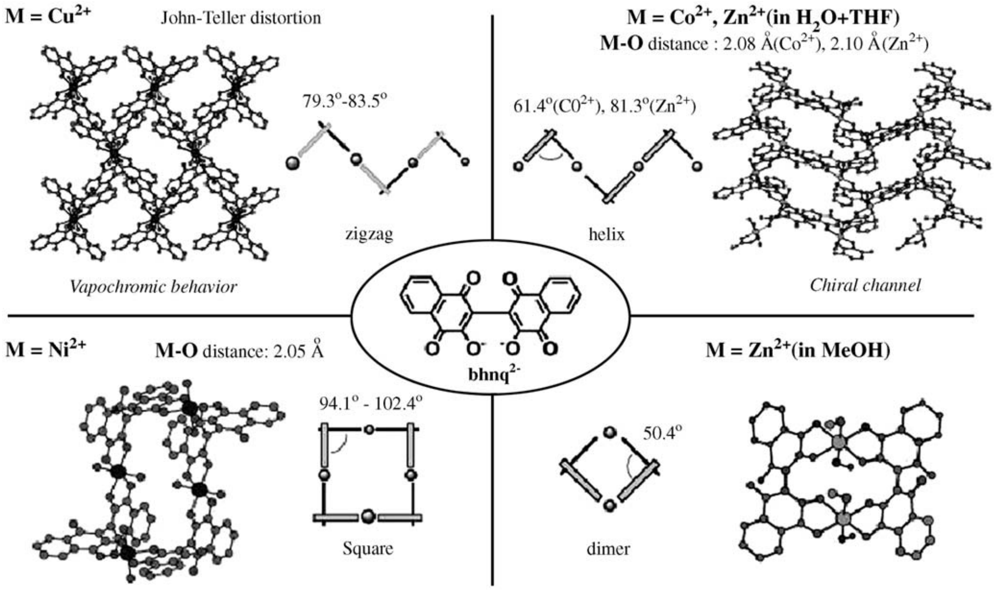


Fig. 1. Different structural families of network solids obtained from the "hinge-like" bhnq^{2-} ligand. Reprinted with permission from Ref. [21].

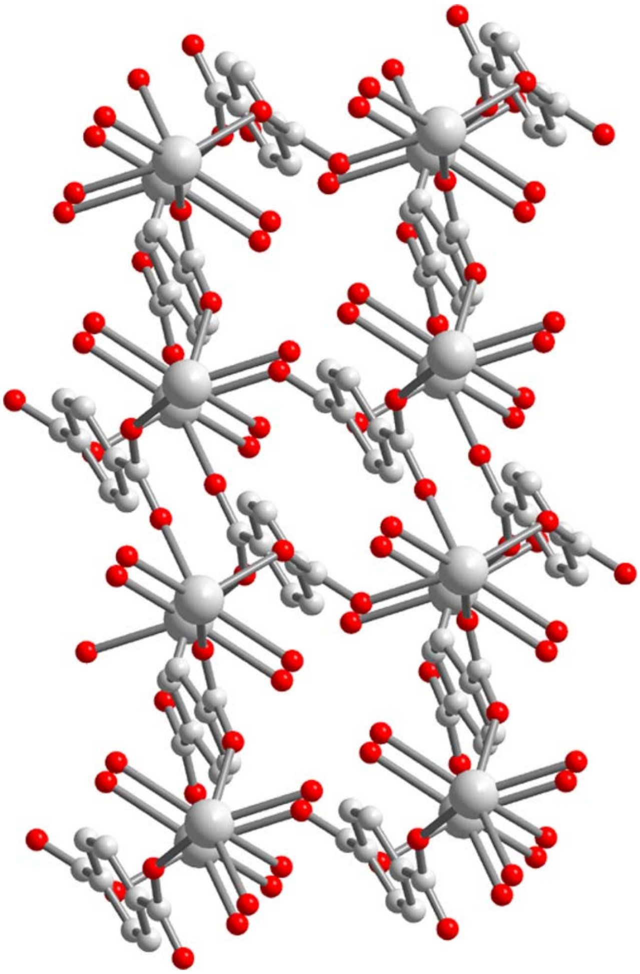


Fig. 2. A fragment of the structure of $Tb_2(terepthalate)_3$, $(H_2O)_4$ showing the open channels with labile water molecules directed into them. Upon removal of water, the structure could resorb NH_3. Adapted from Ref. [26].

metal centers to retain a stable framework despite having lost a ligand was very significant to the function of these solids and stems directly from the adaptable coordination sphere of the Ln ion. Similarly, stability to desolvation was observed with the Yb(III) complex of 1,2,4,5-benzenetetracarboxylic acid (btec) which formed a pillared layered solid shown in Fig. 3. The geometry of the tetrasubstituted benzene core enforced a structure wherein two types of btec ligand bridged four and six metal ions, respectively. The structure sustained partial loss of water. At higher degrees of desolvation, long-range order was lost but this could be regained upon resolvation. Finally, to illustrate more structural variation, with a small but still rigid spacer such as fumarate or maleate, in the presence of hydroxide ion, very unusual 1-D inorganic sub-networks cross-linked by the dicarboxylates in the remaining two dimensions can result with lanthanides [29].

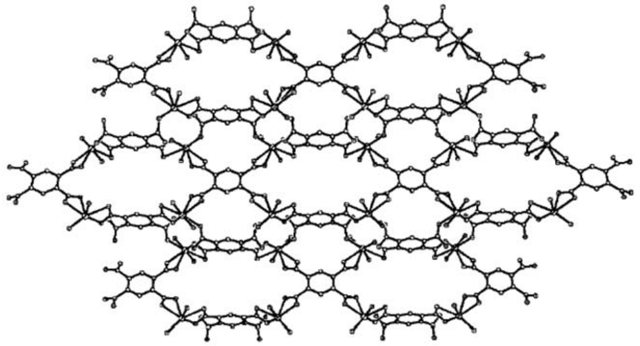


Fig. 3. The structure of $[\{Yb(btec)_{1/4}(btec)_{3/6}(H_2O)_2\}_4 6H_2O]_n$ as reported in Ref. [28]. Channel guests removed for clarity.

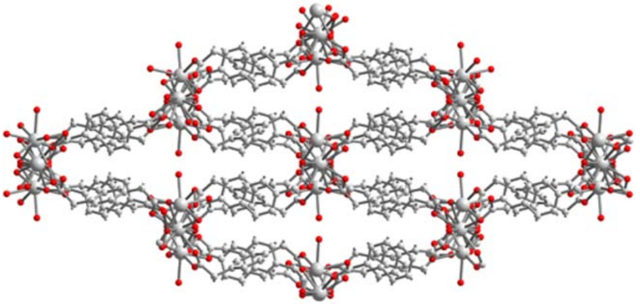


Fig. 4. The structure of $[Er_2(phenylenediacetate)_3(H_2O)]$ with guest water molecules removed for clarity [30]. 1-D inorganic columns are formed rather than layers which are then cross-linked into a 3-D network.

3. Systems with two adaptable components

Staying with lanthanide carboxylate examples, if the rigid spacers in the previous systems are replaced with more flexible linkers, thus forming an adaptable metal/adaptable spacer pair, significant changes can result. With lanthanide ions and phenylenediacetic acid, 1-D helices comprise the inorganic skeleton [30]. These units are then cross-linked by the flexible organic spacers into an open framework solid shown in Fig. 4. This compound, possessing two adaptable components, could desorb and resorb water but, most notably, could size-selectively absorb CO_2 over Ar or N_2.

Another option for two adaptable components would be to have both adaptable metal and ligating functionalities but employ rigid spacers. Our research group has prepared numerous Ag^+ sulfonate solids. Silver(I) is a d^{10} ion often observed in linear, trigonal, or tetrahedral geometries as well as five- and six-coordinate geometries. As mentioned, the sulfonate group can adopt numerous bridging modes which lie within energetically similar domains. With respect to structurally dynamic solids, to date, the largest structural transformation we have observed is in [Ag(3-pyridinesulfonate) (MeCN)] [31].Upon loss of the MeCN by heating, the solid

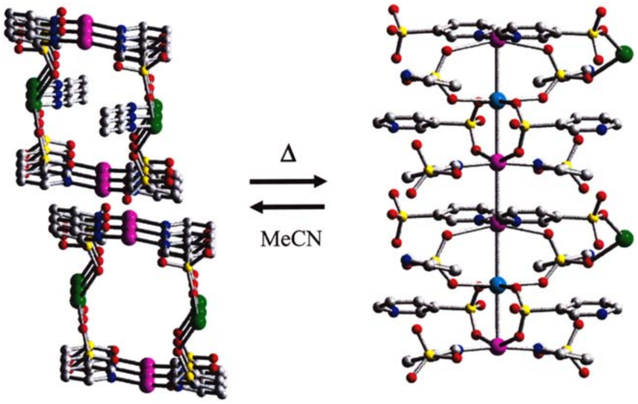


Fig. 5. Reversible transformation from the solvated triclinic phase of [Ag(3-pyridinesulfonate)] to the tetragonal desolvated phase [31]. MeCN solvent has been deleted from the lower left part of the image.

converted from a 3-D triclinic to 3-D tetragonal crystal system requiring major rearrangements to occur in the solid (Fig. 5). The proposed mechanism for this involved cleavage of silver–sulfonate interactions but not any of the stronger Ag–pyridine bonds. During this transformation, the involved silver(I) centers lost contact with sulfonate oxygen atoms (2.4–2.7 Å) but would simultaneously gain ligation to other sulfonate oxygen atoms in the solid. Thus, the ability of the SO_3 group to access several bridging modes and the pliant coordination sphere of silver(I) were critical to this process. Addition of MeCN restored the network with retention of crystallinity.

Another previously mentioned aspect of adaptability is the formation of new inorganic motifs. In a study varying the breadth of rigid aryl substituents in layered silver(I) RSO_3 complexes [32], it was found that the lateral width of the R group could not exceed 6.4 Å if a simple hybrid inorganic–organic motif was to be retained. Importantly, R groups exceeding this value did not result in discrete aggregates but other infinite frameworks where the Ag–SO_3 aggregation motif had shifted to 1-D columns and additional Lewis basic interactions (either solvent or Ag–π interactions) were formed to maintain the extended structure.

Organosulfonate and Ba^{2+} ions, a heavier alkaline earth ion typically with coordination number 7–9 and an irregular geometry, form another adaptable assembly pair. These compounds are generally much more robust than their silver(I) counterparts. Topotactic dehydration/rehydration processes are typical rather than exceptional for these solids. A representative example is $[Ba_2(\alpha, \alpha', \alpha''\text{-mesitylenetrisulfonate})(H_2O)_2]\cdot Cl$. This pillared layered solid demonstrated two transitions to new ordered phases with dehydration and remained ordered to 420 °C [33]. The TGA and variable temperature PXRD data are shown in Fig. 6. The mesitylene unit was an ideal pillar for this layered material and defined channels capable of accommodating Br^-, Cl^- and F^-. Notably, this compound displayed highly efficient anion exchange. Exchange F^- for Cl^- ions was observed even in the presence of only a stoichiometric amount of F^-. With respect to adaptability, the fact that numerous ligating modes of a sulfonate group exist in a small energetic window has been mentioned and this is manifested in the facile topotactic dehydration/rehydration of this solid. This insoluble solid immediately precipitated from solution, upon combining $BaCl_2$ and the sulfonate ligand, as a single-phase microcrystalline product. This phase was found to be identical to crystals which required hydrothermal growth. This fact reinforced that the assembly of the ionic components in solution was readily optimizable. Similar behavior with respect to both single-phase rapid precipitation, high stability, and topotactic dehydration was observed in the formation of Ba tironate [34]. Upon loss of water, this material could resorb H_2O and H_2S selectively.

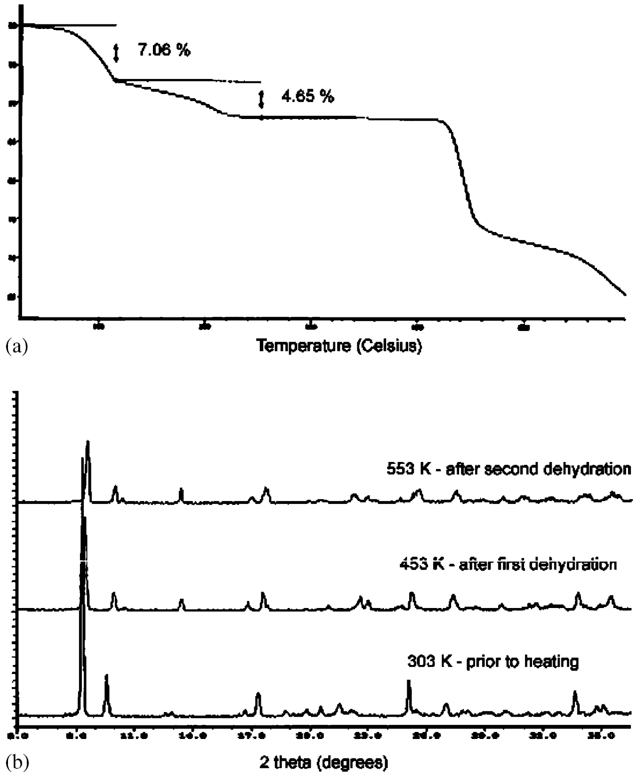
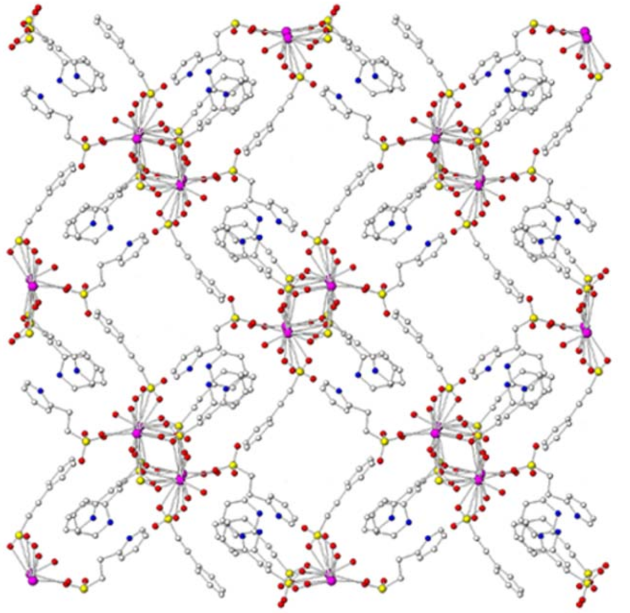


Fig. 6. (a) TGA data showing two dehydration steps for $[Ba_2(\text{mesitylenetrisulfonate})(H_2O)_2]\cdot Cl$ and stability to 420 °C. (b) VT-PXRD traces showing the sample is not only stable but ordered after the two dehydration steps in (a).

Ba sulfonates also illustrate that, with adaptable components, the organic moiety can play a greater structure-directing role. This is germane to the second advantage mentioned for assembling adaptable components, that being the formation of new structures. Despite a lack of structural evidence, most barium sulfonates have been assumed to be layered solids leading to their use as lubricants [35]. With a fairly simple organosulfonate such as 2-pyridylethanesulfonate and an appropriate guest (EtOAc), 1-D columns of $BaSO_3$ aggregation can be obtained [36]. While this compound converted to a microcrystalline lamellar solid upon heating, it did serve to show that the tendency for Ba sulfonates to form layered solids was not overwhelming. Indeed, going to a larger and more rigid spacer, with tetrakis(4-sulfophenyl)adamantane, the first example of discrete clusters of $BaSO_3$ aggregation was obtained [37]. Both compounds are shown in Fig. 7. This layered network was composed of Ba_4–$(SO_3)_6$ clusters, bridged by ligands functioning as tripods, where three of the four sulfonate groups participated in cluster formation thus leaving one SO_3 group uncoordinated. The structure represented a compromise between the coordinative tendencies enforced on the network by the ligand geometry and that dictated by the metal–ligand coordination.



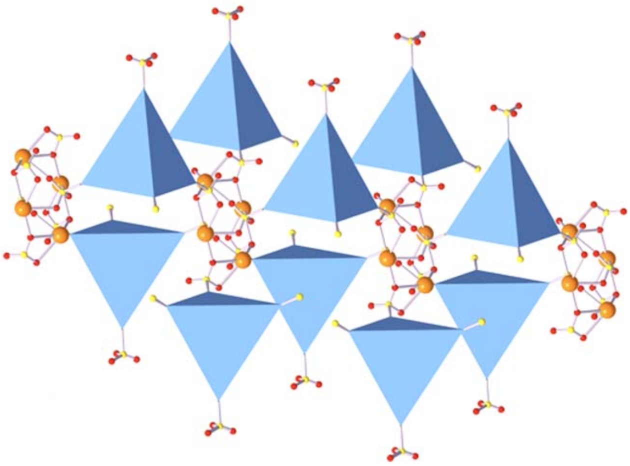


Fig. 7. The top image depicts the 1-D channels formed by Ba(2-pyridylethanesulfonate)$_2$ · EtOAc with guests removed [36]. The lower image shows the 0-D Ba_4 clusters formed by Ba_2(tetrakis(4-sulfophenyl)adamantane) [37], where the pyramids represent the tetraphenyl adamantane units.

In a similar vein to barium sulfonates, lanthanide phosphonates could be regarded. Much more work has been done in this area largely under the umbrella of forming layered solids or 3-D motifs by pillaring of these layers [38]. Lanthanides have similar ligating properties to the heavier alkaline earths in that they have high coordination numbers with irregular geometries. An open grid, layered solid has been reported for the Ln complexes of a tetraphosphonated binaphthyl ligand [39]. In these structures, Ln atoms as vertices, each linked four different binaphthyl ligands, to form a 2-D open rhombic grid which then stacked in the third dimension (Fig. 8). Each Ln vertex was 8-coordinate incorporating four molecules of water in its coordination sphere. Upon dehydration, the network transformed to an amorphous phase but notably, the parent structure could be reformed upon exposure to water vapor, illustrating that while long-range order was lost, the local coordination environment was maintained. While the nature of the amorphous material is not commented on at length in this work, most likely, the structure has shifted to enable increased ligation of the Ln ions by the phosphonate groups. Thus, the combination of adaptable metal ion and ligating group had allowed the framework to alter its structure in response to the dehydration while still accommodating the Ln coordinative requirements. An additional element of adaptability was illustrated in this work in that the phosphonate groups existed in different degrees of protonation. There were two tetraphosphonate ligands per formula unit, one existed in a doubly protonated form and the other in a triply protonated form.

Very recently, the structure of a carboxyphosphonate ligand, *N*-phosphonoethyl-piperidine-4-carboxylic acid, with Ln ions was reported [40]. This solid was composed

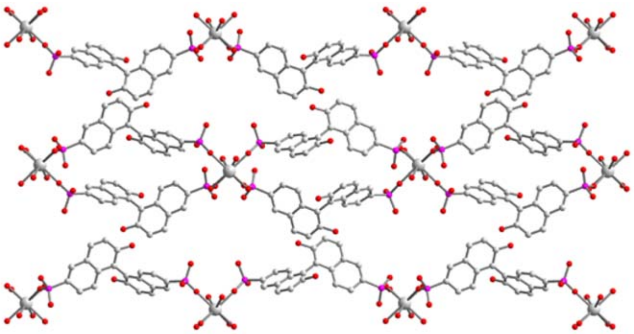


Fig. 8. The rhombic grid formed by the Ln tetraphosphonate complexes in Ref. [39]. Ethyl groups of the ethoxy substituents have been removed.

of Ln ions bridged into 1-D columns by the phosphonate groups and cross-linked by the carboxylates into a 3-D network incorporating water in micropores. As in the previous example, structural changes occurred with desorption of water but the nascent structure was regenerated upon exposure to water vapor. This example represented the first carboxyphosphonate or diphosphonate framework to show anything other than a pillared layered structure and illustrated the new topologies attainable using adaptable components.

The fact that weaker, more adaptable bonding is employed in the formation of a solid does not preclude highly thermally stable compounds. In cases where the spacer unit enables the formation of a simple dense phase, exceptionally stable solids have been observed. A layered Eu structure, which is stable to 573 °C, has been reported containing both 1,4-benzenedisulfonate and 4-sulfobenzoic acid as pillars. Though the degree of order retained in the solid is not commented on, this thermal stability is quite remarkable [41]. Another example, as a more qualitative illustration of the lattice energies attainable using adaptable metal and ligating groups is that barium 4,4′-biphenyldisulfonate will precipitate preferentially to barium sulfate [42].

4. Systems with three adaptable components

The previous examples have dealt with the combination of adaptable ligating groups and adaptable metal ions linked by rigid spacers. With regards to the formation of adaptable solids, the use of solids where all three components can be considered adaptable may, at first glance, offer options for a highly flexible solid. In fact, from the small pool in the literature where the metal, ligating group and linker all possess adaptable features, it seems, in actuality, this is a good recipe for the formation of a dense, static and highly robust solid as there are too many degrees of freedom. For example, in the case of the carboxyphosphonate, $Pr[O_3P(CH_2)_3CO_2]$, a dense layered solid was formed which was ordered to 500 °C [38].

5. Summary

The purpose of this article has not been to propose definitive guidelines for MOF syntheses but rather, it is an attempt to shift notions regarding what building units merit consideration for such structures. With justification, efforts are being made to define rules for the synthesis of inorganic solids [2–4]. Fundamental to these efforts is the goal of making syntheses predictable which then inherently relies upon well-defined interactions between well-defined building units. The goal of this article has been to illustrate that assembly units which do not meet the criteria above should not necessarily be disregarded as ill-defined or unreliable, but rather their versatile coordinative tendencies should be recognized as beneficial for the formation of adaptable solids. Indeed, in several works it is commented on (almost to the authors' own surprise) that a functional solid could be obtained *despite* the use of assembly units with less well-defined assembly properties. This work has not been intended to imply that a dynamic or adaptable solid is attainable exclusively when less well-defined components are employed as there are numerous examples of dynamic solids sustained by "all-rigid" interactions [43] as labeled above [8], however, the use of such components should not be precluded when, in fact, their assembly properties should actually favor dynamism in solids.

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