Inorganic Structures and Nets in Metal–Organic Frameworks (MOF)

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Abstract | An overview of the metal–organic framework structures of many different dimensionalities and types have been described based on simple linkages involving node and rings, which have their origin in mathematics. The variety and diversity exhibited by these compounds showcase the usefulness of the topology based description of structures. In addition, hypothetical structures have also been discussed to provide pointers for future researchers.

1. Introduction

New materials based on the supramolecular assembly of metal ions and organic ligands, often known as coordination polymers (networks) or metal–organic frameworks (MOFs), continues to evince interest from researchers investigating in basic as well as applied aspects. This area of research has attracted the attention due to the possibility of preparing new compounds that can incorporate the many functionalities offered by the organic chemistry. Persistent research by many groups during the past decade or so, gave rise to a large variety of compounds exhibiting a plethora of properties, both traditional as well as new ones.[1] In spite of the many advances over the years, we have only a rudimentary knowledge about the structure–property correlations in this system of compounds and in this context an understanding of the structural aspects at a molecular level would be beneficial.[2]

The aluminosilicate zeolites, which are the foremost example of open structures, have been studied extensively.[3] Their structures have been understood based on simple building units known as the secondary building units (SBUs).[4] Such studies on MOF structures are beginning to emerge.[5] One of the important developments in this direction has been the use of simple mathematical relationships in periodic three-dimensional systems by considering points, lines etc.[6,7] This approach introduced the usefulness of nodes or connecting points in the description of structures. Thus, a vertex sharing tetrahedra can give rise to a variety of three-dimensional structures based on 4-connected nets.

In MOFs, the coordination around the central metal ion could vary considerably and require deeper insight for the structural understanding. Such a situation would utilize the commonalities of the binding nodes and the principles of net formation in a more general way and help in our understanding. Though the concept of node and net are of mathematical origin, they are not abstract entities but represent real chemical structures. The earlier work in this direction is due to Wells,[7] who compiled a large number of possible nets that represent both realized structures as well as yet to be discovered ones.

The metal–organic framework structures have its origin in inorganic coordination chemistry and consist of easily accessible polyhedral units. The geometrical diversity can, then, be used to visualize a large number of possible nets and in select cases provide possible clues to target a particular network topology.[8] Thus, a combination of coordination geometrical preference of the metal ion along with the differences in the binding mode of the organic ligands can be exploited to result in a variety of structures. Some of the observed MOF structures

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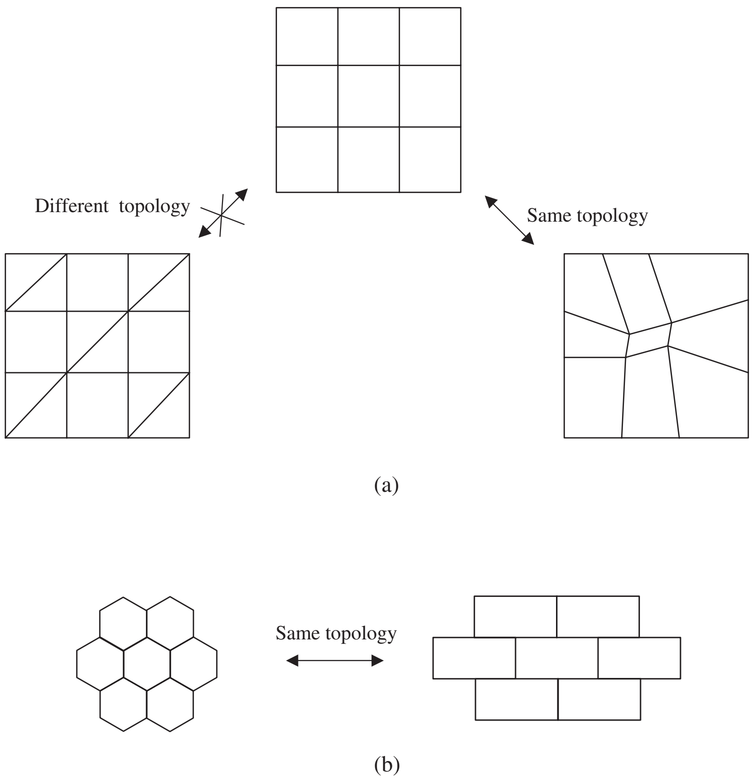
Figure 1: Illustrative examples of identical and different topologies from similar nodes: (a) $4^4$and (b) 6^3.



represent well known nets such as diamond,[9] α-Po,[10], NbO[11] etc. lattices.

In this article, we attempt to provide an insight into the family of metal–organic frameworks from the point of view of classical inorganic structures and network topologies. In doing so, we have taken cognizance of the important structural aspects and expanded the scope by providing clues for designing new structures using the idea of network topologies/connectivities. Though it is difficult to provide examples of all the possible structural and topological types, efforts have been made to include illustrative examples of some of the key members that represent classical structures.

1.1. *Node and Net – how are they related?*

A node is a series of points representing a particular geometry (tetrahedral, octahedral etc) and can be used for the description of a structure. The node is generally connected to a fixed number of related points that depends on the geometry (tetrahedral = 4; octahedral = 6). The structures that result from such connectivities can, then, be represented mathematically as either a discrete (zero-dimensional) or an infinite (one-, two and three-dimensional) periodic arrangements known as nets. Thus, a net can be considered as an extended representation of the node and define the structures using the polyhedral connectivity as the basis.[12] The analysis of a net based representation also helps in making a solid with pre-defined structure and possibly properties via self assembly. This implies that both directional bonding (hydrogen, covalent, coordinate bonds) and shorts-range interactions ($\pi \ldots \pi$, CH$\ldots\pi$ etc.) may be of importance in controlling the formation of the structure. A study of the relative energies of the various solids clearly indicates that the covalent bond based structure would require the highest energy of formation. It is possible to conceive and observe closely related network structures wherein the net connectivity may be the same, especially during the transformation of structures by squeezing, bending or stretching manipulations without breaking any of the bonds (Figure 1).

As noted above, the net topology, is based on the number of nodes.[7] According to Wells, a path is considered by sequential connection of the node. When the path starts and ends with the same node it is known as the circuit.[7] A net would, then, be considered by determining the shortest circuit which goes through the node. This is generally known as the fundamental ring.[7,12]

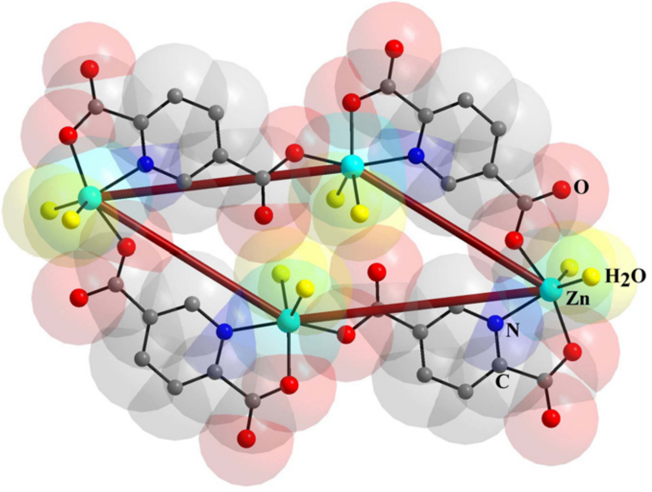


Figure 2: The zero-dimensional molecular box structure in $[Zn_2(H_2O)_4][C_5H_3N(COO)_2]_2$.

Wells defined a net with only one type of a ring and a node by the notation (n,p), where p is the number of the links at the node and n is size of the smallest ring.[7] The net which results from such connectivties are generally known as uniform nets. This type of notation has been found to be useful in describing the two- as well as the three-dimensional nets. Thus, the graphite structure has a two-dimensional (6,3) net and the diamond structure is a three-dimensional (6,4) net. A more generalized notation can be conceived which would include a variety of nodes and rings within a net. This can be represented as

$$\begin{pmatrix} m & & p \\ n & , & q \\ \ldots & & \ldots \end{pmatrix}$$

in which all the possible combinations of nodes and rings have been included. From this, a net with two types of rings and one node can be represented as

$$\begin{pmatrix} m & & \\ & , & p \\ n & & \end{pmatrix}$$

and a net with one ring and two nodes as

$$\begin{pmatrix} & & p \\ n & , & \\ & & q \end{pmatrix}$$

These are special cases and are simple in nature. When complex nets are encountered, a different nomenclature can be considered. These are in the form, $A^{X1}.B^{X2}.C^{X3}\ldots$ where the letters A, B, C… are the size of the smallest circuit originating from that ring (n). The superscripts X1, X2… represent the number of circuits at the node. Although the connectivity of the node, p, is not included, it may obtained from the sum of the superscripts:

$$\text{Thus, } \Sigma Xi = p(p-1)/2\ldots \qquad (1)$$

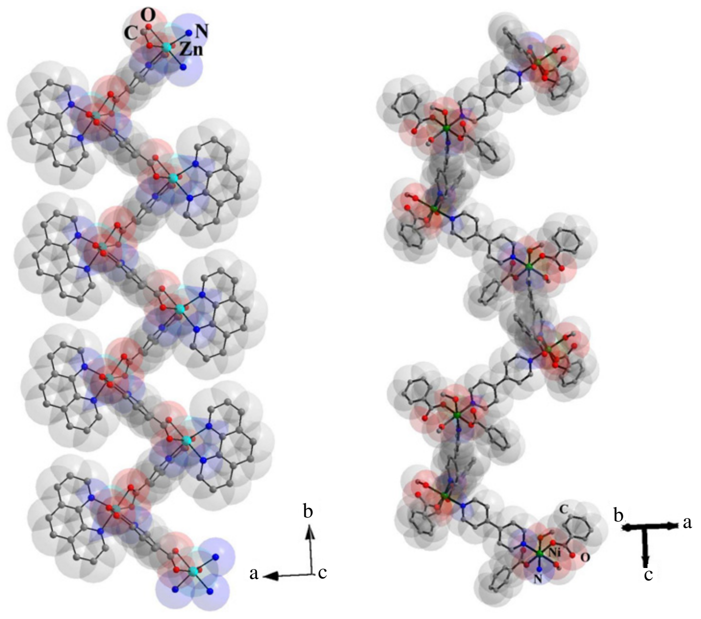
Solving this for p, gives

$$p = 1/2 + (1/4 + 2\Sigma Xi)^{1/2}\ldots \qquad (2)$$

The total number of circuit is determined by considering all the possible link pairs formed at the node. For example, a 3-conected node with the links a, b and c has 3 pairs: ab, bc, and ac, and in the general case the number of linked pairs is equal to $p(p-1)$ as in equation (1) and the connectivity$p$ is given by equation (2). This type of notation is known as Wells point symbol, Schläfli symbol or short symbol, and applying this we will get 6^6 net for diamond, but the diamond net is also described as 6^4 net.

A three-letter code, similar to that employed to designate a particular structure in the family of aluminosilicate zeolite structure,[12] has also been proposed for MOF structures. The three-letter code follow a particular structure type, for example, the $SrSi_2$-net is named **srs** and the quartz net **qtz**. Other rationalization for certain codes also exits, such as **pcu** (from primitive cubic packing) for the α-polonium net. The codes form a set of well-defined names and help in the use and retrieval of structure type from a database search.

Figure 3: (a) The one-dimensional zig-zag structure in $[Zn(C_{12}H_8N_2)][C_5H_3N(COO)_2].0.5H_2O$. (b) The one-dimensional helical structure in $[Ni(4,4'\text{-bipy})(ArCOO)_2(CH_3OH)_2]$ (Ar = C_6H_5, 2-$(OH)C_6H_4$, 3-$(NO_2)C_6H_4$).



(a) (b)

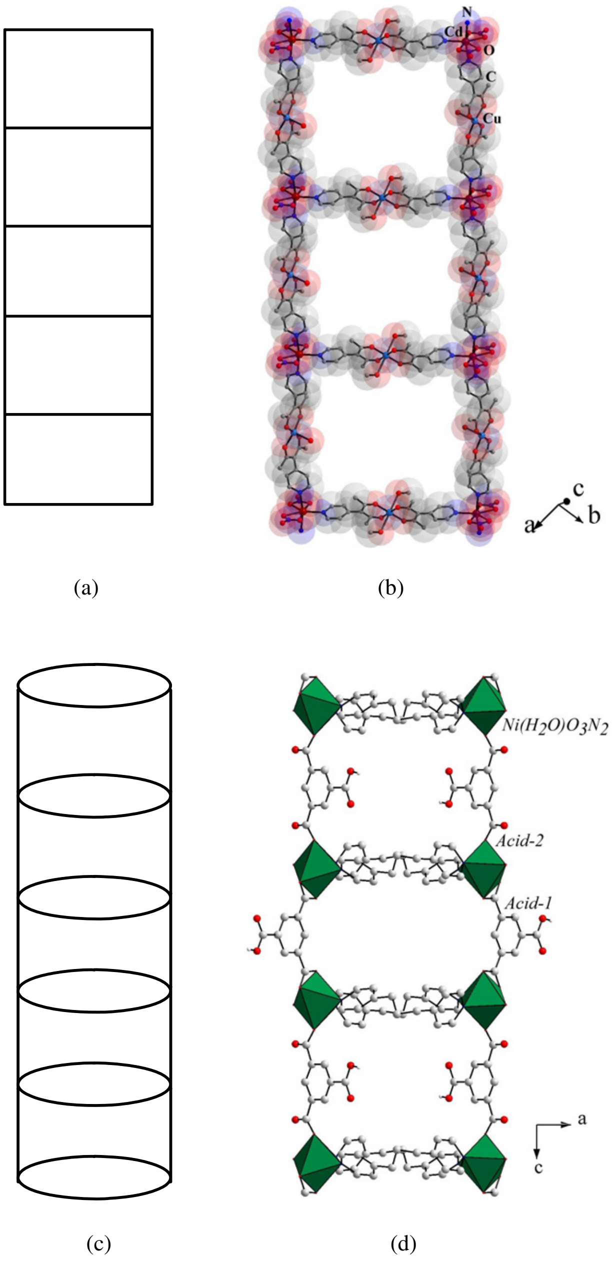
1.2. *Zero-dimensional structures*

Simple molecular complexes have been known for many years. But from the perspective of understanding structure only few are relevant. There are instances where the principle of self assembly have been employed for the design and the isolation of zero-dimensional structures. Examples of such structures include the molecular square[13] and, more recently, spheroid structures[14] of high nuclearity and molecular weight. A molecular tetrameter of square (rhombus) type structure, $[Zn_2(H_2O)_4][C_5H_3N(COO)_2]_2$, with connectivity between Zn^{+2}ions and the pyridine-2,5-dicarboxylate anions has been isolated (Figure 2).[15] The structure, with the shape of a molecular box, consists of four Zn^{+2} cations and four carboxylate anions. The terminal water molecules along with the presence of terminal C–O bonds gives rise to a large number of significant O–H…O hydrogen bonds. The hydrogen-bond interactions between the molecular box units form an extended two-dimensional structure. In this two-dimensional structure, the molecular square box unit acts as the building block to form the two-dimensional square grid (4^4 topology) through hydrogen bond interactions. The molecular structures of this type have been considered important towards our understanding of the formation of higher dimensional ones. The zero-dimensional structures are also useful for generating the other infinite structures described herein.

1.3. *One-dimensional topology*

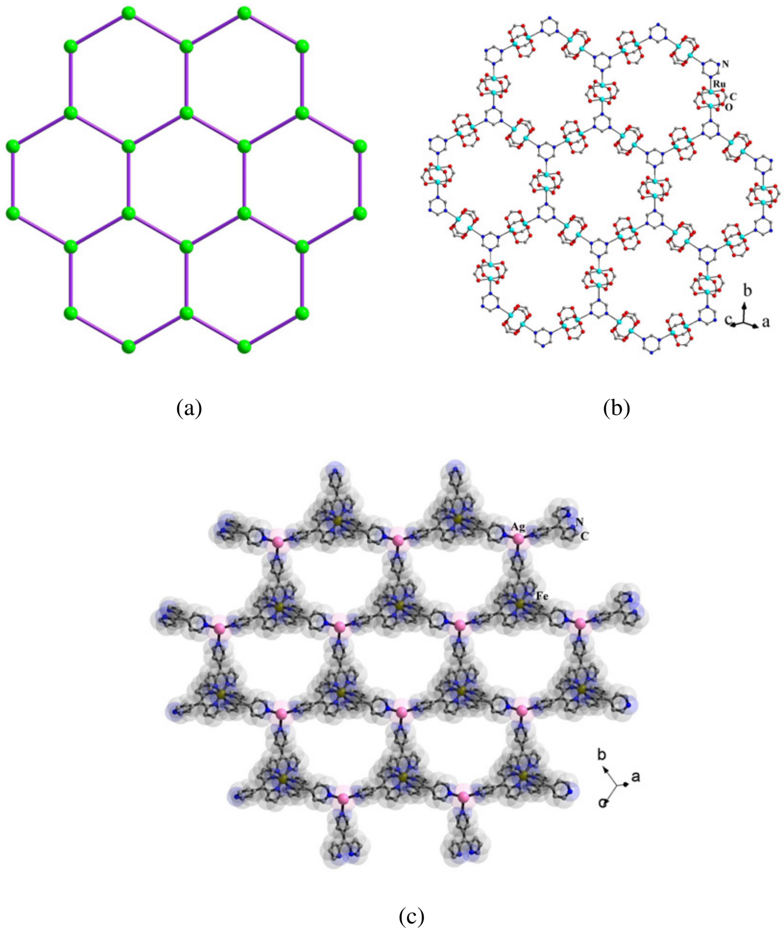
The one-dimensional structures are generally based on simple zig-zag chain, helical chain, ladder or tubular arrangement. The arrangements between the one-dimensional structures differ due to the organic linkers (spacer) that are present in them. The one-dimensional structures pack efficiently using weak secondary interactions such as hydrogen bonding, $\pi \ldots \pi$ interactions and give rise to robust higher-dimensional structures.[16] Two one-dimensional compounds, $[Zn(C_{12}H_8N_2)][C_5H_3N(COO)_2].0.5H_2O$, and $[Zn(C_{12}H_8N_2)][C_3HN_2(COO)_2]$, have zig-zag structures stabilized by efficient $\pi \ldots \pi$ interactions (Figure 3a).[15] $[Ni(4,4'\text{-bipy})(ArCOO)_2(CH_3OH)_2]$ (Ar = C_6H_5, 2-$(OH)C_6H_4$, 3-$(NO_2)C_6H_4$),[17a] has helical arrangement (Figure 3b).[17] A one-dimensional ladder-like structure differ from the zig-zag and the helical structures.[18] The building unit is effectively a 'T-shaped' moiety, which can also contain cavities depending on the length, shape and orientation of the connecting ligand. A good example of a molecular ladder is $[M(L)_{1.5}(NO_3)_2]$ (L = bipy or bis(4-pyridyl)ethane).[19] A mixed metal ladder structure, $[Cd(NO_3)_2]_2[Cu(Pyac)_2]_3(CH_3OH)_3(THF)_{1.5}$, (Pyac = bis[3-(4-pyridyl)pentane-2,4-dionato], THF = tetrahydrofuran) where the Cu sites are coordinated by solvent molecules

Figure 4: (a) A schematic of the one-dimensional ladder structure (b) The one-dimensional ladder structure in $[Cd(NO_3)_2]_2[Cu(Pyac)_2]_3(CH_3OH)_3(THF)_{1.5}$, (Pyac = bis[3-(4-pyridyl)pentane-2,4-dionato], THF = tetrahydrofuran). (c) A schematic of the one-dimensional column structure. (d) The one-dimensional column structure in $[Ni(C_{13}N_2H_{14})(H_2O)][C_6H_3(COO)_2(COOH)]$ ($C_6H_3(COOH)_3$ = trimesic acid, $C_{13}N_2H_{14}$ = 1,3-bis pyridyl propane).



and exposed to the pores (Figure 4a and 4b).[20] A one-dimensional structure, $[Ni(C_{13}N_2H_{14})(H_2O)][C_6H_3(COO)_2(COOH)]$ ($C_6H_3(COOH)_3$ = trimesic acid, $C_{13}N_2H_{14}$ = 1,3-bis(pyridyl) propane), with a column like structure has also been reported (Figure 4c and 4d).[21] In this structure the connectivity between the metal centre and the trimesate forms one-dimensional wire-like arrangement. Two spacer ligand units connect with the metal units forming a column-like arrangement, which are organized three-dimensionally via O–H…O hydrogen bonds. One-dimensional structures of the general formula, $[M_2(H_2O)_2(C_{14}H_8O_4)_3]$ (M = Nd, Dy, Y),[22]

Figure 5: (a) A schematic of the two-dimensional 6^3topology (honeycomb). (b) The two-dimensional structure of $[\{Ru_2(PhCOO)_4\}_3(trz)_2]$ (trz = triazine). (c) The two-dimensional 6^3 structure of $\{Fe(4\text{-pyrdpm})\}\{Ag(X)F_6\}$.Solvent] (M = Co, Fe; 4-pyrdpm = 5-(4-pyridyl)-4,6-dipyrrinato, X = P). Note that in (b) and (c) the net has a 6^3 topology.



which mimic the structure of the mineral tancoite, $[LiNa_2H][Al(PO_4)_2(OH)]$,[23] has also been reported. The one-dimensional structures have been discussed as part of this article to provide an insight into the possible variety in MOF structures. The main theme of this article, however, is to identify and arrange the two-and the three-dimensional structures within the family of MOFs using the network topology. The zero- and one-dimensional structures are presented for the sake of completion, though they are not typically based on any net connectivity.

1.4. *Two-dimensional networks*

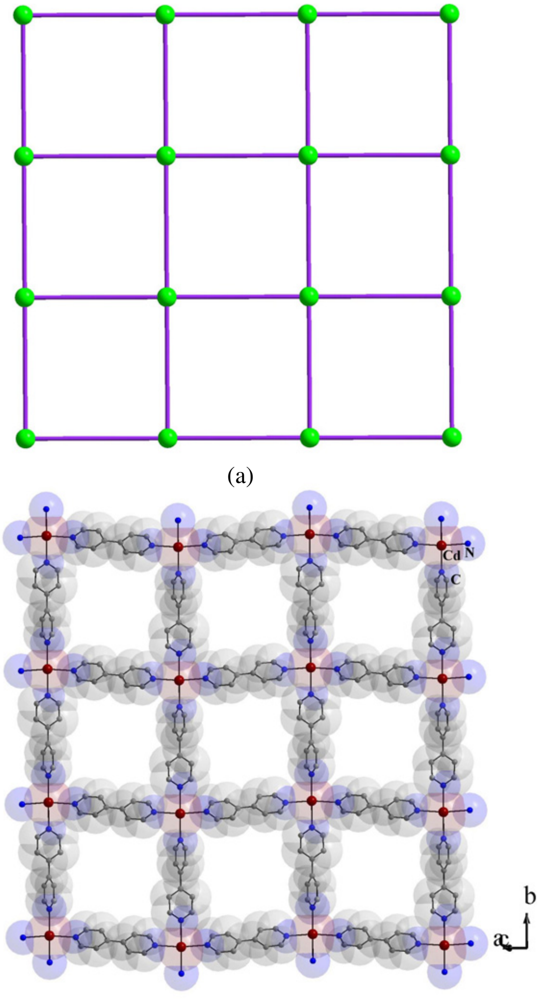
The use of linear bifunctional spacer ligands has yielded many two-dimensional MOF structures. The ratio between the metal and the ligand along with the nature of the coordination of the ligands are important in determining the structural topology of the network. The use of simple building units such as triangles, squares and hexagons generally result in a 2D network since three hexagons, four squares and six triangles with angles of 120, 90 and 60°, respectively, meet at a node in a two-dimensional network. The Schläfli symbols for this topological arrangement are designated as 6^3, 4^4, and 3^6, respectively.

The graphite structure represents the ideal example for a two-dimensional structure with a 6^3 topology. This topology, also known as the honeycomb net, is common in supramolecularly assembled organic structures due to the availability of trigonal nodes (i.e., 1,3,5-trisubstituted benzenes such as trimesic acid and the related amine).[24] In the family of MOFs, the first 6^3 topology was described by Zaworotko and co-workers in $Cu_2(pyrazine)_3SiF_6$.[25] Many other examples of the 6^3 topology are also known in MOF.[26] Kitagawa and co-workers prepared a two-dimensional MOF,

$[\{Ru_2(PhCOO)_4\}_3(trz)_2]$ (trz = triazine),[26a] in which two Ru^{+2} ions are connected with four benzoate anions forming a neutral paddlewheel complex,$[Ru_2(PhCOO)_4\}_3]$. Triazine molecules connect this unit to form the two-dimensional structure with the 6^3 topology. In this, the paddlewheel diruthenium center act as the linker and the triazine acts as the three-connected node to form the honeycomb structure (6^3 topology) (Figure 5a and 5b). A two dimensional 3d–4f mixed metal pyridine-2,3-dicarboxylate, $[Gd(H_2O)_3Co(pydc\text{-}2,3)_3]$ (pydc-2,3 = pyridine-1,3-dicarboxylate) with a honeycomb network has been reported.[26b] In this, the nine coordinated Gd^{+3} ions and the six coordinated Co^{+3} ions are connected by pyridine-2,3-dicarboxylate to form the two-dimensional layers, with both the metal ions acting as nodes forming the honeycomb topology. Compounds with the general formula, $\{M(4\text{-pyrdpm})\}\{Ag(X)F_6\}$.Solvent] (M = Co, Fe; 4-pyrdpm = 5-(4-pyridyl)-4,6-dipyrrinato, X = P, Sb), also have a two-dimensional structure with 6^3 topology.[26c] In this, the M^{+3} ions (M = Co, Fe) are coordinated by the three 4-pyrdpm anions forming a neutral complex, [M(4-pyrdpm)], which are further connected by Ag^+ ions to form the two-dimensional layer with 6^3topology using two different types of nodes (M and Ag) (Figure 5c).

Two-dimensional structures based on the 4^4 network topology exemplify a particularly simple and commonly observed net in the family of metal–organic frameworks. The 4^4 topology can be classified into three different types – square grid, rhombus grid and rectangular grid according

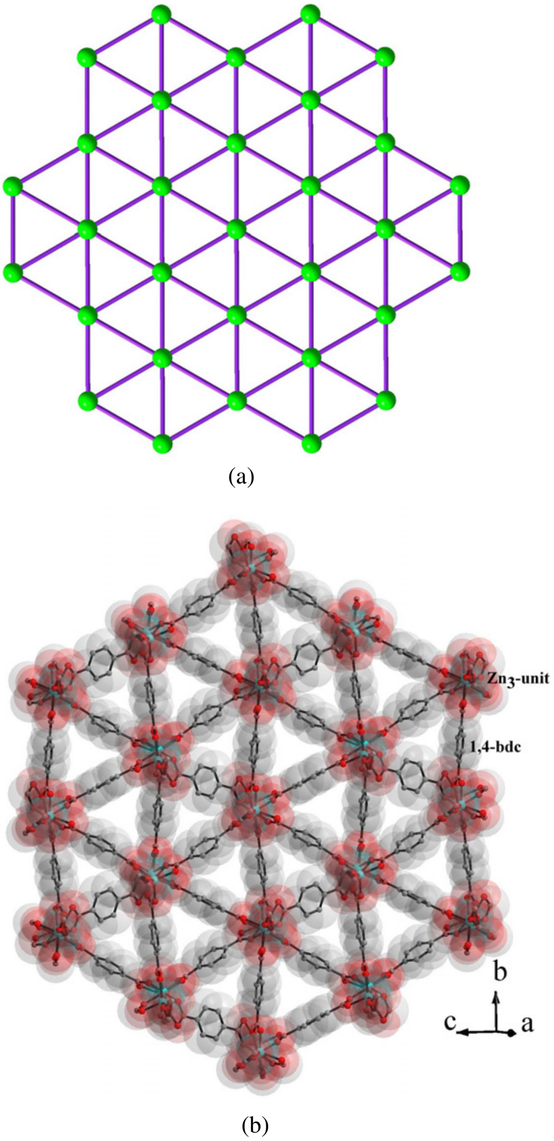
Figure 6: (a) A schematic of the two-dimensional 4^4 topology (square grid). (b) The square grid topology in $[\{Cd(4,4'\text{-}bpy)_2\}(NO_3)_2]$.



(a)

(b)

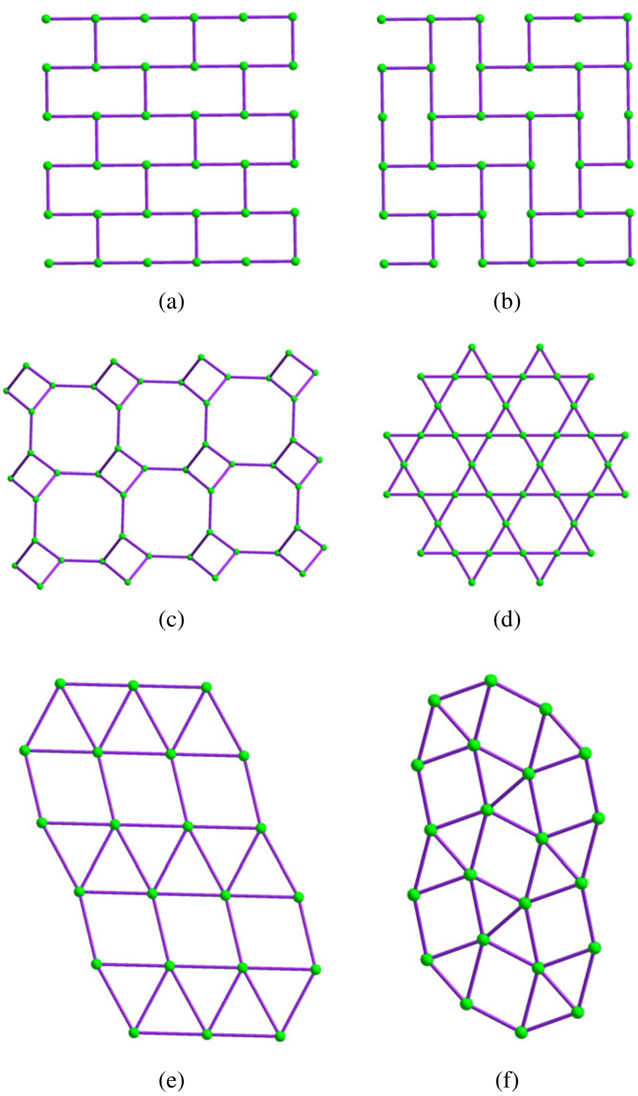
Figure 7: (a) A schematic of the two-dimensional 3^6 topology. (b) The two-dimensional structure of $[Zn_3(1,4\text{-bdc})(DEF)_2]$.DEF (1,4-BDC = terephthalate).



to the nature of the angle and the length of the two sides within the fundamental ring. The fundamental ring, on the otherhand, depends on the nature of the coordination geometry around the metal ions and the length of the ligands. The foremost example typically illustrating the 4^4 network topology was obtained using the cyano bridges.[27] This family of structures have been expanded by including pyrazines,[28] bipyridine[29] and other analogues of bipyridine.[29a, 29d, 30] Simple square grid with open networks have been generated with bipyridine as the ligands by Fujita et al.[31] in $[\{Cd(4,4'\text{-bpy})_2\}(NO_3)_2]$ (Figure 6). This structure was confirmed by preparing a clathrate complex with o-dibromobenzene, $[\{Cd(4,4'\text{-bpy})_2\}(NO_3)_2(C_6H_4Br_2)_2]$.[31] The same topology was also observed with a number of transition metals, such as Co^{+2}, Ni^{+2}, and Zn^{+2}.[32] Two types of spacer ligands in $[M(4,4'\text{-bipy})(pyca)(H_2O)][NO_3]$ (M = Co, Cd; pyca = pyridine-4-carboxylate), forming a rectangular grids have been known.[29f, 33] Rhombus grid topology has also been observed using the spacer ligand, 4,4′-azobipyridine, which is bent.[29a]

MOFs with 3^6 topology are less common when compared to the 6^3 and 4^4 topologies. The first example of the 3^6 topology was described by Schröder and co-workers in $[Zn_3(1,4\text{-bdc})(DEF)2]$.DEF (1,4-BDC = terephthalate)

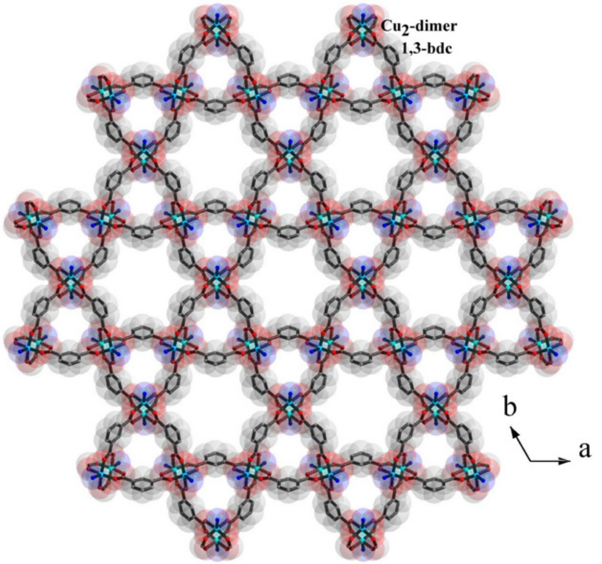
Figure 8: Schematic of the various possible two-dimensional dimensional topologies: (a) brickwall, (b) herringbone, (c) $4^1 8^2$, (d) $3^2 6^2$ (Kagome), (e) and (f) $3^3 4^2$.


(a) (b) (c) (d) (e) (f)

(Figure 7).[34] In this structure, three Zn^{+2} ions are connected by 1,4-benznedicarboxylate to form the two-dimensional layer. DEF, used during the synthesis, are bonded with Zn and satisfies the coordination requirement. Each of the Zn_3 unit is connected with six 1,4-bdc and each 1,4-bdc are connected with two Zn_3-units forming a two-dimensional network of 3^6 topology. The same topology has also been observed in $[Zn_3(SDA)_3(DMF)_2]$ (SDA = trans-4,4'-stilbenedicarboxylate).[35]

To form the three types of topologies, described above, the nodes necessarily must have 3-, 4- and 6-fold rotational symmetry. Figure 8 shows the topologies that can be generated by varying the angles around a node. 3-connected nodes with angles of 180, 90 and 90° result in brickwall or herringbone like structure (Figure 8a and 8b), which also retain 6^3 topologies.[18a,29a,36] Another 3-connected 2D net with angles of 90, 135 and 135° give rise to a network with $4^1 8^2$ topology (Figure 8c).[37] Similarly, 4-connected nodes with angles of 120, 60, 120 and 60° give rise to networks with $3^2 6^2$ topology (Figure 8d). This network is commonly known as the Kagome lattice. Kagome lattice with transition metal occupies an important position for the study of magnetic interactions. Such triangular arrangement of magnetic ions are expected to show high level of magnetic frustrations.[38] In MOF compounds, this topology was first observed in

Figure 9: The two-dimensional Kagome structure ($3^2 6^2$ topology) topology in [{$Cu_2(py)_2(1,3\text{-bdc})_2$}$_3$] (py = pyridine; 1,3-bdc = isophthalate).



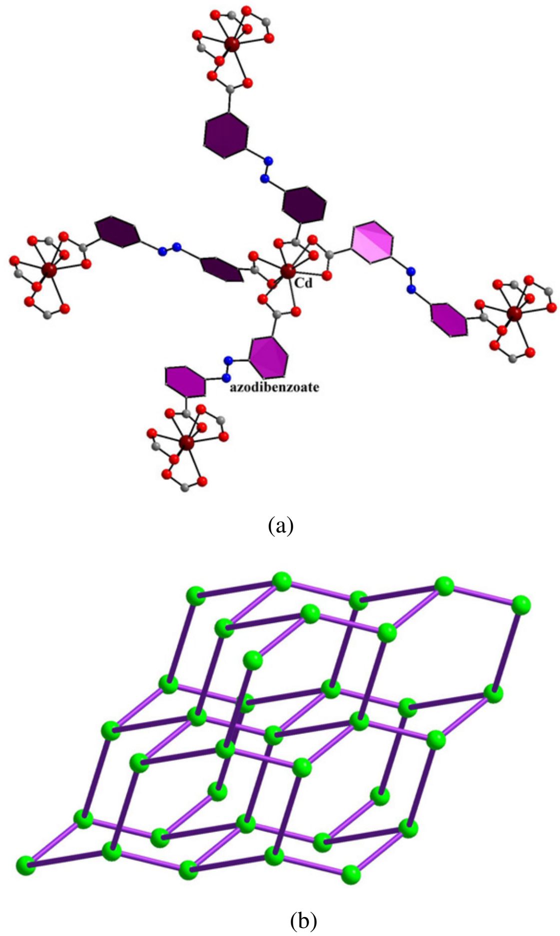
[{$Cu_2(py)_2(1,3\text{-bdc})_2$}$_3$] (py = pyridine; 1,3-bdc = isophthalate) (Figure 9).[39] Kagome-like topologies, though few, have been observed in other MOFs and related systems as well.[40] 5-connected nodes with angles of 90, 60, 60, 90 and 60° form two different networks both of which comprise $3^3 4^2$ topologies (Figure 8e and 8f). The topology of the first type (Figure 8e)[41] was observed in [$La(NCS)_3(L)_{2.5}$] (L = meso-1,2-bis(ethylsulfinyl)ethane) and the second type (Figure 8f)[42] was observed in [$M(H_2hedp)(H_2O)$].$3H_2O$ (M = Y, Tb; H_5hedp = etidronic acid).

1.5. *Three-dimensional networks*

The three-dimensional structures represent a higher level of complexity, compared to the two-dimensional ones. The understanding of such topological networks are important for the practioners of crystal engineering to obtain reasonable control and predictability of the structural arrangement. In this section, the common three-dimensional structures of the MOF compounds that contain (mimic) some of the well known inorganic structures would be presented. It may be noted that the larger the number of available structures, the easier it would be to analyze and catalogue the framework topology. It is likely that there may be nets that would exhibit close relationships with the ideal nets and in some cases the structural arrangement would be distorted. It is important that the rules laid out for the description of a particular network structure is not violated.

One of the commonly observed three-dimensional net is the Diamond net based on tetrahedral connectivity. They are also called as diamondoid network structures.[1e,43] The diamondiod topology is important as many compounds formed with this topology exhibit non-linear optical properties (NLO), which requires a non-centrosymmetric space group. The diamond net does not have inversion centres at the nodes and the structures are, therefore, often acentric. A large number of building units have been utilized for arriving at the diamondoid related networks, which shows the ubiquitous nature of this structure.[44] The diamond net is uninodal, four connected with tetrahedral nodes and contain six-membered rings. The compounds of [Cu(2,5-dimethylpyrazine)$_2$(PF_6) and [Cu(4,4'-bipy)$_2$][PF_6)] represents the earliest examples of a metal–organic compounds exhibiting diamondoid structure.[44a] In [Cd(3,3'-azodibenzoate)$_2$(H_2NMe_2)(NH_4)],[45] each Cd^{+2} ions are connected with four other Cd^{+2} ions through four 3,3'-azodibenzoate linker and the Cd^{+2} ions act as the tetrahedral node (Figure 10a). The arrangement of Cd^{+2} ions form the diamond net (Figure 10b). Replacing the 3,3'-azodibenzoate ligands by a simple linear bond gives rise to adamantane-type unit, which is also characteristic of the diamondiod networks. The Cd–Cd–Cd angles are in range 92.7–123.2° which indicates a significant distortion from the ideal tetrahedral angle of 109.5° found in diamond.

Figure 10: (a) The connectivity between Cd^{+2} ion and 3,3′-azodibenzoate linkers in [Cd(3,3′-azodibenzoate)$_2$(H_2NMe_2)(NH_4)] (Cd^{+2} ion acts as the tetrahedral node). (b) The connectivity between Cd^{+2} ions through 3,3′-azodibenzoate forming the diamond net. The Cd^{+2} ions and the 3,3′-azodibenzoate linkers are represented as green spheres and linear bonds, respectively.

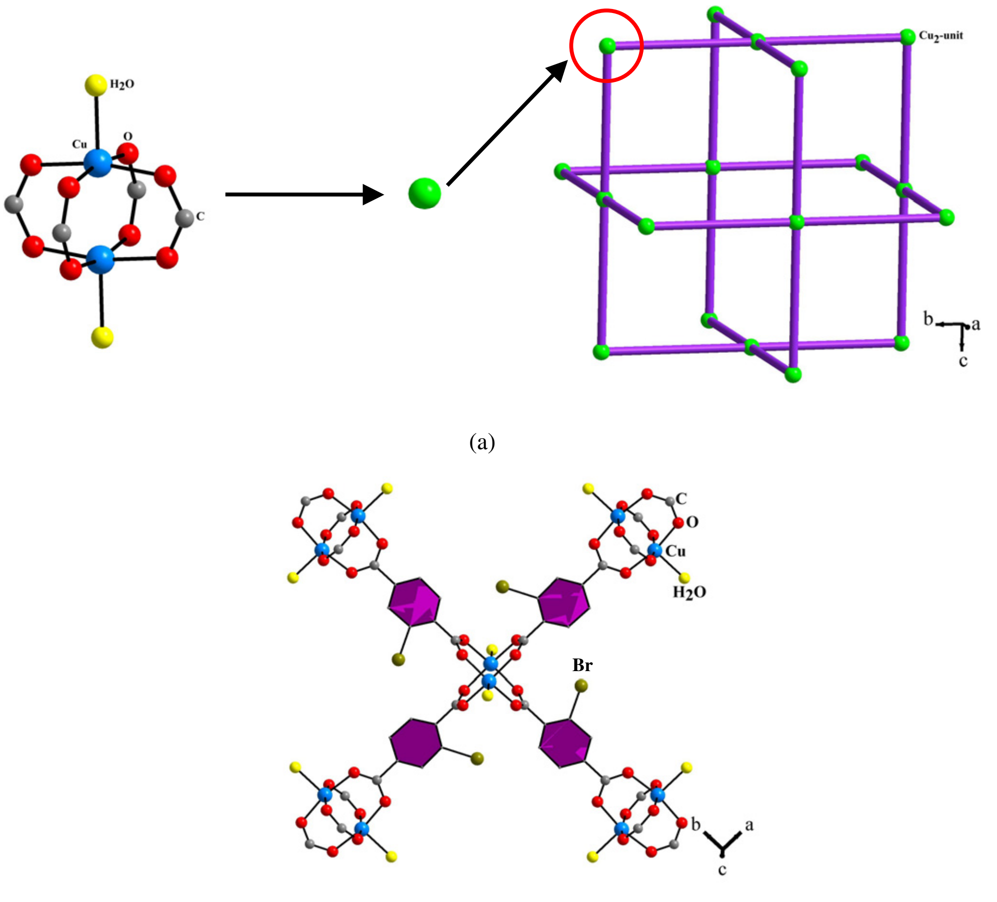


The niobium oxide (NbO) is the second most common four-connected net (after diamond), which is built from perpendiculary oriented square planar units.[11,46] The linkages at the node may not necessarily be the same due to the coordination variations of the central metal atom. This net has been observed in compound possessing five-coordinated Cu(II), existing in distorted square-pyramidal geometries,[46a,46b,46c] or in octahedral compounds with two non-bridiging axial ligands.[46d] A good example of this net is [Cu_2{o-Br-bdc}$_2$(H_2O)$_2$].8DMF.2H_2O (o-Br-bdc = 2-bromo-terephthalate),[11] where $Cu_2(COOO)_4(H_2O)_2$ unit act as the four connected node which are connected by the 2-bromo-terephthalate anions (Figure 11).

$CdSO_4$ represent another type of three-dimensional structure based on four connected net.[47] The structure is different compared to the NbO net as the smallest rings in $CdSO_4$ structure is a hexagon and not an octagon as found in NbO structure. In addition, only half of the neighbouring rings are related by a 90° turn. In $CdSO_4$ the two similar layers are arranged perpendicular to each other. This topology was observed in a series of rare-earth based MOFs with the formula, [M_2(2,2’-bipy)$_2$(1,3-bdc)$_3$].2H_2O (M = Y, Gd, Dy; 1,3-bdc = isophthale).[48] In this structure, two MO_6N_2 units are connected by the carboxylate anions forming a paddle wheel like unit (Figure 12a), which are connected with 1,3-bdc anion forming the three-dimensional structure, which is identical to the $CdSO_4$ network (Figure 12b).

Boron nitride net represents a simple 5-connneted topology derived by the cross-linking of hexagonal 2D layers with the 6^3 topology.[49] In [Eu_2{$C_{10}H_{14}(COO)_2$}$_3$],[49c] the Eu^{+3} ions are connected with 1,3-adamantanedicarboxylate

Figure 11: (a) Figure shows the connectivity between the Cu_2-units and 2-bromo-terephthalate anions to form NbO net $[Cu_2\{o\text{-}Br\text{-}bdc\}_2(H_2O)_2]$.8DMF.$2H_2O$ (o-Br-bdc = 2-bromo-terephthalate). The Cu_2-units and 2-bromo-terephthalte anions are represented as green spheres and linear bonds, respectively. (b) The connectivity between the $Cu_2(COOO)_4(H_2O)_2$ unit and 2-bromo-terephthalate.



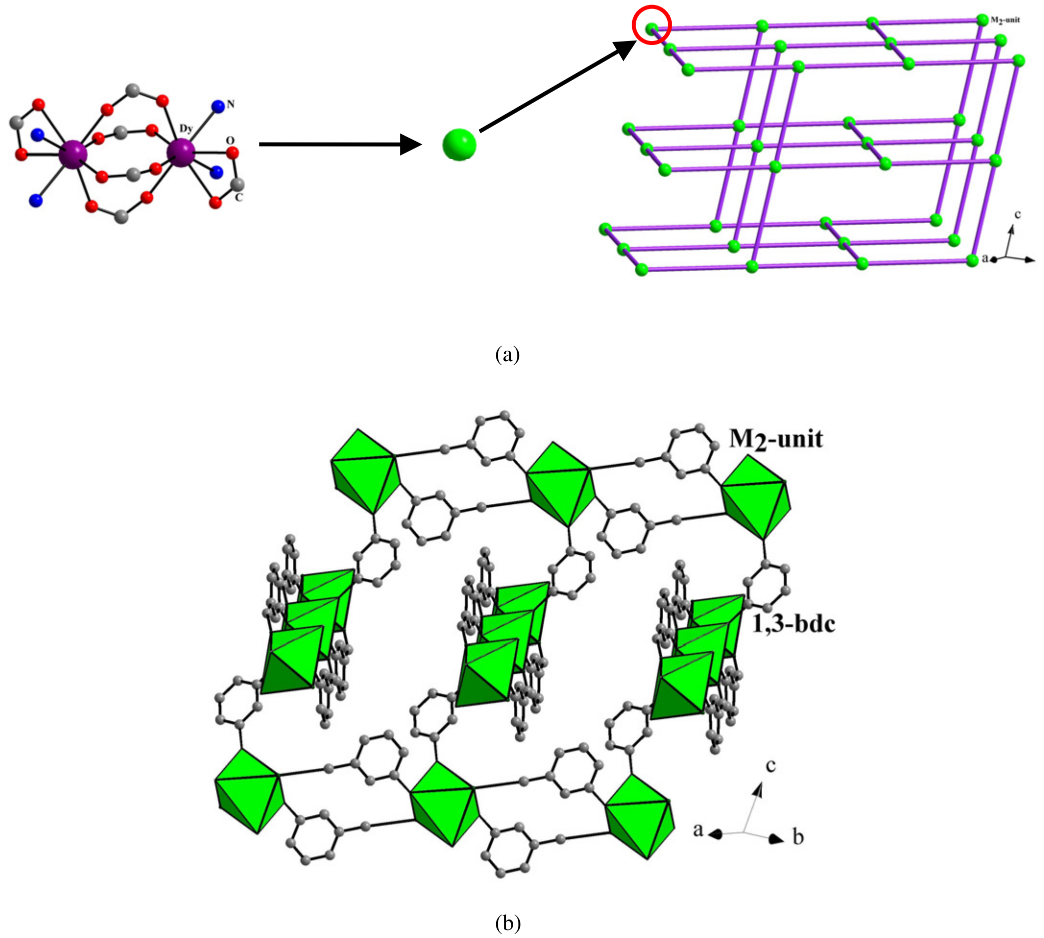
(a)

(b)

forming two-dimensional hexagonal layers. The layers are cross-linked by the face-sharing of the europium polyhedra forming the 3D structure (Figure 13). As can be noted the Eu atoms actually act as nodes forming the boron nitride topology.

Another simple net that can be considered is based on the 6-connected α-Po structure. The α-Po net can be created by linking the octahedral metal centres by a simple linear 2-connecting ligands. Thus, six ligands are attached to each metal and two metals are attached through each ligand. The Prussian blue family of solids belongs to this net.[50] A net of this type can be readily visualized by employing the 2-connecting ligand, 4,4'-bipyridine. It may be noted the same ligand was also employed for the generation of 4-connected 2D square grid (Figure 6). This ligand and other related ones have been used extensively for the preparation of a variety of two- and three-dimensional nets. Ligands based on a simple benzene rings appears to be not compatible with the α-Po net, as accommodating six independent 6-membered N-heterocycles such as pyridine around the central octahedral metal could lead to considerable steric strain.[51] The octahedral metal centres, however, readily accommodates six 5-membered N-heterocyclic donor ligands such as imidazole.[51] The more recent approach for the visualization of this topology is to consider polynucler metal cluster units as the 6-connected nodes, which connect with six other similar cluster units using aromatic carboxylate ligands. A wide variety of compounds with this network topology have been prepared by Yaghi and co-workers.[10] Figure 14 shows the structure of $[Zn_4O(1,4\text{-}bdc)(DMF)_8(C_6H_5Cl)]$ (MOF-5),[52] where Zn_4O cluster unit act as a six connected node linked by 1,4-bdc forming the α-Po topology. It is clear that the α-Po topology has a primitive cubic arrangement.

Figure 12: (a) Figure shows the connectivity between the M_2-units (M = Dy) and isophthalate anions to form $CdSO_4$ net in $Dy_2(2,2'\text{-bipy})_2(1,3\text{-bdc})_3].2H_2O$ (1,3-bdc = isophthalate). The M_2-units and isophthalate anions are represented as green spheres and linear bonds, respectively. (b) Figure shows the three-dimensional structure of $[Dy_2(2,2'\text{-bipy})_2(1,3\text{-bdc})_3].2H_2O$ through the connectivity of paddle-wheel unit and isophthalate (1,3-bdc).



(a)

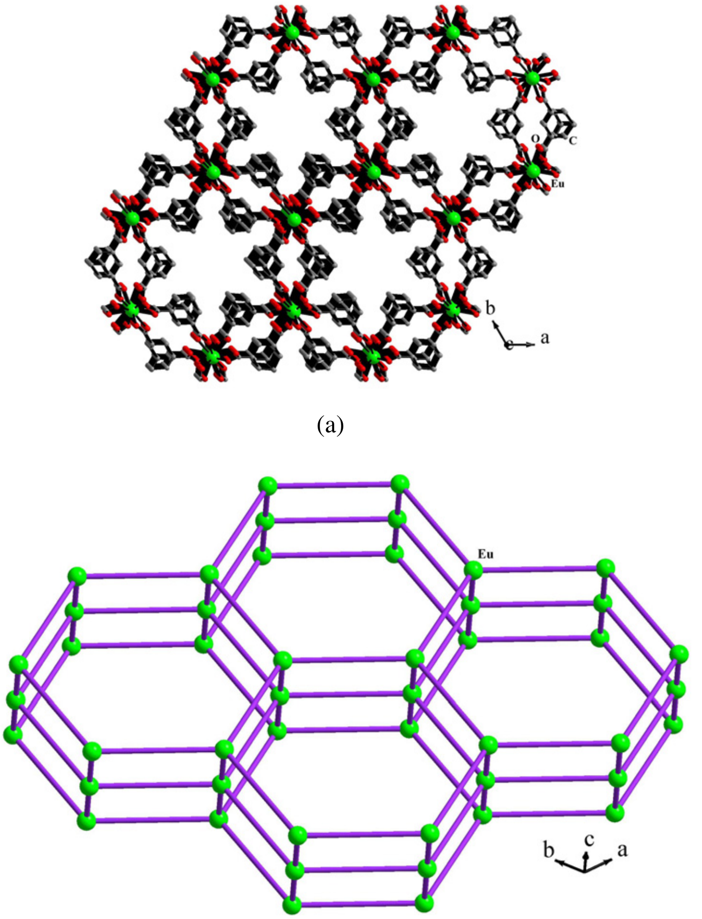
(b)

1.6. *Future possibilities*

Based on the descriptions and discussion of the variety of structures here, one can readily envision the formation of a large variety of other related structures. In this light, the MOF structures are highly versatile since the coordination ability of the organic ligands can be varied along with the presence of the central metal ions. In this review, we consider some of the network structure that are possibly based on the available and known ones. There are hypothetical structures and as yet no known examples exit in the literature. We will present here some examples of network topology which can be formed in the context of MOF structures by using suitable metal ions and organic ligands.

Figure 15a shows the pictorial view of a two-dimensional network based on the connectivity between three, four and six membered ring with $3^1 4^2 6^1$ topology. MOF structure with this type of topology can be formed by the connectivity between the metal ions and small organic acids such as formic acid, acetric acid etc. Metal organic framework with long organic ligand such as 1,3-bis(pyridyl) propane and related organic ligand can also form this type of topologies. It is known that the use of long organic ligands can lead to interpenetrated structure due to availability of lager six membered rings. MOF structures based on the connectivity between four and six membered rings are also not known in the literature. Here, we have shown two types of possible networks with $(4^1 6^2)(4^2 6^2)$ and $(4^1 6^2)(6^4)$ topologies (Figure 15b and 15c). Compared to the $3^1 4^2 6^2$ topology (4-connected), here two different types of nodes are present (3- and 4-connected). Transition metal ions

Figure 13: (a) Figure shows the connectivity between the Eu^{+3} ions and the 1,3-adamantanedicarboxylate anions in [$Eu_2\{C_{10}H_{14}(COO)_2\}_3$]. (b) The connectivity between Eu^{+3} ions according to their connectivity. Note the formation of BN topology by the 5-connected node of the Eu atom.



(a)

(b)

can, generally, act as 3-connected node and benzene-1,2,4,5-tetracarboxylate can act as the 4-connected node to form the two-dimensional structure with this type of network.

Recently, the classical inorganic structure, the perovskite topology has been reported in a three-dimensional MOF, $[(CH_3)_2NH_2]Zn(HCOO)_3$,[53] where $(CH_3)_2NH_2^+$, Zn^{+2} and $HCOO^-$, respectively act as A, B and X to maintain the general formula of the perovskite, ABX_3. In this context, one can look at mixed metal MOFs such as 3d–4f, 3d–4d, 3d–5f etc.[54] to form perovskite type topology. Similarly MOF structures with spinel (AB_2X_4) and pyrochlore ($A_2B_2X_7$) topology can also be considered with suitable choice of ligands and metal centers. Though it is difficult to predict the possible outcome of such manipulations in the formation of these types of complex structures, but it is obvious that the bridging ligands should be adequately designed with the necessary functional groups to facilitate favorable interactions. The future in this area of designer framework solids appears to hold much promise and one can look forward to the exciting possibility of preparing new compounds with many fancied properties.

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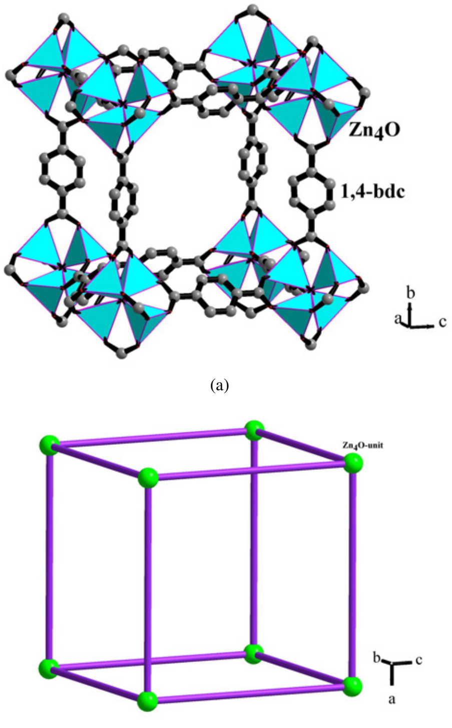
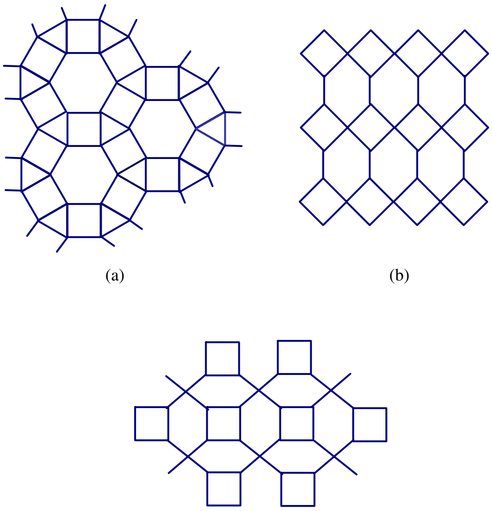
Figure 14: (a) The connectivity between Zn_4O clusters and terephthalate anions forming the 3D structure in $[Zn_4O(1,4\text{-bdc})(DMF)_8(C_6H_5Cl)]$. (b) The connectivity between Zn_4O clusters and terephthalate anions. Note the formation of α-Po (pcu) topology. The Zn_4O units and terephthalate anions are represented as green sphere and linear bonds, respectively.



(a)

(b)

Figure 15: Schematic of the possible two-dimensional networks with three different nodes: (a) $3^1 4^2 6^1$; (b) $(4^1 6^2)(4^2 6^2)$; (c) $(4^1 6^2)(6^4)$.



(a) (b)

(c)

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