Review

Supramolecular Coordination Assemblies Constructed From Multifunctional Azole-Containing Carboxylic Acids

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Abstract: This paper provides a brief review of recent progress in the field of metal coordination polymers assembled from azole-containing carboxylic acids and gives a diagrammatic summary of the diversity of topological structures in the resulting infinite metal-organic coordination networks (MOCNs). Azole-containing carboxylic acids are a favorable kind of multifunctional ligand to construct various metal complexes with isolated complexes and one, two and three dimensional structures, whose isolated complexes are not the focus of this review. An insight into the topology patterns of the infinite coordination polymers is provided. Analyzed topologies are compared with documented topologies and catalogued by the nature of nodes and connectivity pattern. New topologies which are not available from current topology databases are described and demonstrated graphically.

Keywords: multifunctional ligands; azole-containing carboxylic acids; coordination polymers; topology

1. Introduction

The assembly, structure and potential applications of metal-organic coordination polymers, especially the Metal-Organic Frameworks (MOFs), as functional materials have attracted extensive attention from researchers worldwide because of their intriguing complicated compositions, versatile framework topologies and interesting properties in gas sorption, optics, magnetism and as supporting
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carriers, etc. [1–7]. At present, the rational synthetic strategy in this field usually involves the use of multifunctional ligands with multiple active coordination sites to prepare the target compound [8–12]. Polydentate ligands can act as either bridging or chelating ligands to link metal ions together, resulting in the desired networks in the final metal organic coordination polymers [13–16].

According to a statistical analysis of the literature over the past decade, multifunctional carboxylate ligands with nitrogen-bearing heterocycles have been used expansively in the synthetic strategies to develop multidimensional (one, two and three dimensional) framework structures. For example, pyridinecarboxylic acid and its analogues with active oxygen and nitrogen sites on the both ends have been successfully applied to synthesize coordination polymers [17–28]. Compared to the above rigid ligands, the relatively flexible and peculiar carboxylic acids derived from the diazole, triazole and tetrazole moieties have come to be regarded as all-purpose ligands in recent years that can potentially coordinate metal ions in various ways, due to their complicated coordination modes and different performance of the N and O ends. The resulting product generally has various structures with distinct topology. A longer and flexible spacer between the N and O end may even result in more complicated topological forms with multiple interpenetrations. These interpenetrating networks of coordination polymers are also an interesting focus of attention currently [29]. For example, the multifunctional ligand terazole-1-acetic acid (Htza) has been used successfully in the synthesis of a series of coordination polymers [30–51] for its variety of coordination styles on the tetrazole and carboxylate group ends. Recently, we and Yu et al. independently and simultaneously synthesized a series of CuII compounds assembled with Htza and published the analysis of their magnetic properties [51,40].

In this paper, our discussion will focus on the topological structure of the MOCNs constructed by the multifunctional carboxylate ligands containing five-membered N-heterocyclic rings (azoles). The azoles in question include 1,2-diazoles (pyrazole), 1,3-diazoles (imidazole), 1,2,3-triazoles, 1,2,4-triazoles and tetrazoles. Over the about past decade, a significant number of metal complexes formed by the title ligands with one-, two-, or three-dimensional framework structures have been reported. Quite many among these are zero-dimensional finite structures, which are not our interest in this work. Most of the zero-dimensional compounds are binuclear. The highest-nuclearity of the reported oligomeric complexes up to now is octanuclear, with cubic structure [52–55]. A summary and discussion for the variety of the topology patterns of the MOCNs assembled by the azole-containing carboxylic acid is contributed to this paper.

**Scheme 1.** The types of azole considered.

![Scheme 1](image)

1,2-diazole (pyrazole) 1,3-diazole (imidazole) 1,2,3-triazole 1,2,4-triazole tetrazole

2. Methodology

Structural data was retrieved from Cambridge Structure Database [56–58] (CSD) up to May 2009. Only azole-containing carboxylic acid ligands in which both nitrogen atoms in the azole ring and
oxygen atom in the carboxylic acid group are coordinated to metal atoms are selected to perform further topological analysis. Nearly three hundred corresponding structures that were published ranging from 1967 to 2009 are listed, in which 81(28%) are zero-dimensional complexes, 71(24%) are one-dimensional structures, 61(21%) are two-dimensional layers and 77(27%) are three-dimensional nets.

In general, MOCNs are constituted by two main parts: the organic linkers and the metal ions. Both metal atoms and ligands are considered as nodes. Coordination bonds are considered as links between nodes. Analysis of topology is performed by using the compiled topology and tiling analytical software TOPOS [59]. As the first step, determination of bonding interactions is calculated by the AutoCN subprogram using the Sectors algorithm in which an improved method of intersecting spheres designed by Peresypkina and Blatov [60] for organic and metal-organic compounds is used. In this method, which is called method of spherical sectors, a sphere of $R_{sd}$ radius is replaced with a set of spherical sectors corresponding to interatomic contacts. The radius ($r_{sec}$) of the $i$th sector is determined by the formula

$$r_{sec} = \left( \frac{3V_i}{\Omega_i} \right)^{\frac{1}{3}},$$

where $V_i$ and $\Omega_i$ are volume and solid angle of a pyramid with basal Voronoi-Dirichlet polyhedron (VDP) face corresponding to interatomic contacts and with the VDP atom in the vertex.

Then both metal atoms and ligands are considered as nodes and the position of nodes that representing clusters or ligands are positioned at the centroids of the group. Coordination bonds are considered as links between nodes. All 0-connected (isolated), 1-connected (dangling) and 2-connected (bridging) nodes are removed to simplify the topology to a maximum extent.

Determination of topology and taxonomy of the simplified nets are analyzed by a subprogram named ADS and searched in the TTD (TOPOS Topological Database) collections for same topological descriptors. The topology of the three-dimensional nets are described by Point Symbol [61], also known as Schläfli Symbol [62], which lists the numbers and sizes of circuits (closed chains of connected atoms) starting from any non-equivalent atom in the net. Instead of Point Symbol, Vertex Symbol, which enumerates the size of faces around each kind of vertex in cyclic order, is adopted customarily to represent topology of two-dimensional sheets. A few exceptions of nonplanar two-dimensional structures, which are two-dimensional but can’t be realized in a plane without intersection of edges, are described by Point Symbol. Known topologies are characterized by RCSR [63] lowercase three-letter symbols, see http://rcsr.anu.edu.au/ for details.

3. One-Dimensional Coordination Chains

3.1. Chain

Single chain is the most preferred one-dimensional structure which can be catalogued into several groups (see Chain in Figure 1): with the title molecules bridging a zigzag chain of metal atoms, one bulky ligand or several small solvent ligands seal the opening of metal atoms. One title ligand links three metal atoms and one metal atom links three ligands, step by step a one-dimensional chain is formed.
The CSD Refcodes presenting in each type of topology are listed below:

| CICZUJ[64] | OGALEO[71] | FEGGAA[78] | MEFZUS[87] | VIKCOI[97] | CEYLOI[104] |
|------------|------------|------------|------------|------------|-------------|
| PIFBAI[65] | OGALIS[71] | FOHFUE[79] | MENGAO[88] | VIQYEA[98] | ECULUK[105] |
| PODZOY[66] | OKEHV[72] | GOYSES[80] | NENDAL[89] | VIQYIE[98] | OKEHIV01[67] |
| AVUPUC[67] | OKEHOB[72] | GOYSIW[80] | NIQQUQ[90] | WUPHEU[99] | RAJNOG[106] |
| AVUQOX[67] | VOBKUT[73] | HIHJIS[81] | PAJJOA[91] | XIBPAA[100] | KOBGUE[40] |
| DOGMAO[68] | BIPJEQ[74] | IDIXOJ[82] | PAJJOA01[92] | XIKWAQ[101] |
| DOGME[68] | DATMUH[75] | IYASEG[83] | PEXSIV[93] | YIFQUZ[102] |
| HUXTUP[69] | DATNAO[75] | LAJZIG[84] | PEXSIV01[94] | TIWRUN[103] |
| NIQWUG[70] | DOGZAB[76] | LAQPAV[85] | QANDUF[95] | KEXWIU[37] |
| OGAKUD[71] | EDURUR[77] | LASSEE[86] | SENJEB[96] | PEXVEU[37] |

### 3.2. Chain and monomer

As a rare case, CEYLEY is an interesting structure of mononuclear complexes of two title ligands and a copper atom are linked by six coordinated tin atoms into a single chain coordinated topology while between chains separated mononuclear complexes bind them into a two-dimensional sql layer by hydrogen bonds (see Chain and Monomer in Figure 1). π-π stacking of diazole rings exists in the piling of layers.

**CEYLEY[104]**

### 3.3. Chains of cubes and rings

Octanuclear oligomer of cobalt atoms and titled ligands are linked by nickel atoms with tetradeinate ring-style ligands into an infinite chain structure that forms a very interesting heterometallic structure (see Chains of cubes and rings in Figure 1).

**WIBNOL[107]**

### 3.4. Ladder

In the ladder structure (see Ladder in Figure 1), metal atoms are 3-connected nodes, where the title ligands are vertical linkers, and small molecules (such as water, oxalic acid) of metal-metal bonds are horizontal linkers. In the DILGIP, POHSUB and VODCEX structures, metal atoms and title ligands serve as two counterpart 3-connected nodes. The vertical linker of PEFVIF is a Second Building Unit (SBU) constituted by a dinuclear complex.

| ABAYEI[108] | XENCEZ[109] | DILGIP[111] | KEPYIO[113] | ROMRUH[115] | LIWLUS[36] |
|------------|------------|------------|------------|------------|-------------|
| AVUQAJ[67] | XOKRIZ[110] | HOSTEO[112] | POHSUB[114] | PEFVIF[116] | VODCEX[43] |

### 3.5. Pipe

Four single chains are linked into one bamboo-like pipe (see Pipe in Figure 1) with the title ligandd as chain linkers and joints of the hollows.

**YIFSIP[102]**
All these topologies are shown in Figure 1.

**Figure 1.** Topology of one-dimensional coordination polymers.

4. Two-Dimensional Coordination Layers

4.1. sql

The uninodal topology sql is a most common one, whose shape is a square grid sheet and has a vertex symbol of \(4^4\))(see sql in Figure 2). Most of the structures of sql topology represent 4-connected metal atoms as vertexes and 2-connected ligands as edges. Both metal atoms and ligands serve as 4-connects nodes in OFITAZ and PEZROC. The structures LIQVEN, YASSEQ, ODIVIH and ODIVON show interweaved sql topology.

| TIGCAO[117] | JEXSIP[120] | LIQVEN[122] | SONJUA[126] | POLDIE[129] | MISHAY[50] |
| EVONOS[118] | KEPYOU[121] | LIWKIM[123] | YASSEQ[127] | KOBGOY[40] | PEZROC[38] |
| HOGDEN[114] | KEPYOU01[68] | OFITAZ[124] | ODIVIH[128] | KOBGOY01[42] | XOHFAM[48] |
| JEDYEX[119] | LAQNUN[85] | OFITAZ01[125] | ODIVON[128] | LIWLOT[36] | XOHPEQ[48] |

**Figure 2.** Topology of the uninodal two-dimensional coordination polymers.
4.2. hcb

hcb is also a very common uninodal planar topology with a vertex symbol of \( \{6^3\} \) and a honeycomb-like shape (see hcb in Figure 2). BOKXUV, FIBJEG, KEKWIH, TIZVI, TIWBAD, VIQZAX, WOFVET and EHAGAW have metal atoms as all 3-connected nodes and ligands as linkers. FENSUN use both metal atoms and the title ligands as 3-connected nodes. NETXI and NOFGAR use the title ligands as 3-connected nodes and metal atoms with terminal water as linkers.

| BOKXUV[130] | FIBJEG[133] | TIZVI[132] | WOFVET[94] | NOFGAR[136] |
| FENSUN[131] | KEKWIH[134] | TIZVI[132] | VIQZAX[98] | NOFGAR[136] |
| FENSUN0[132] | TIZVI[132] | TIWBAD[132] | NETXI[135] | EHAGAW[137] |

4.3. fes

fes is a \( \{4.8^2\} \) topology planar structure with one type of 3-connected nodes. All fes structure is formed by both the title ligands and metal atoms serve as 3-connected nodes and one or two terminal waters on the metal by the side of a two-dimensional sheet (see fes in Figure 2).

| FENSUN[138] | OFIV[125] | TIWBAD[132] | YELIY[140] |
| FENSUN0[92] | OEXP[139] | YELIY[92] | LIMNOL[35] |

Figure 3. Topology of binodal two-dimensional coordination polymers.

4.4. kgd

Topology kgd has a vertex symbol of \( \{4^3\}_2\{4^6\} \), with two type of nodes, 3-connected and 6-connected nodes. All structures with kgd topology in this research have the same ligands and configuration in which the ligand serves as a 3-connected node and metal atoms as a 6-connected node (see kgd in Figure 3).

| JEXSAH[120] | JEXSEL[120] | SEYVEY[141] |

4.5. gek1

gek1 is a binodal two-dimensional topology in personal.ttd database in the TTD collection with the vertex symbol of \( \{3.4.6\} \{3.4.6.3.6\} \) (see gek1 in Figure 3). TIKWUG is basically a title ligand bridged
metal-acetic acid chain which is constructed of 5-connected cadmium atoms and 3-connected titled ligands and 2-connected acetic acids.

4.6. New two-dimensional topologies

Six new topologies which are not present in the TTD collection are listed below (Shown in Table 1).

Table 1. New Two-Dimensional Topologies.

| CSD Refcode | Topology Demonstration | Vertex Symbol* | Nodal Connectivity | Node Types |
|-------------|------------------------|----------------|--------------------|------------|
| UFETEF[143] | ![Topology](image)     | \(\{4^3.6^3\}\) | 4-c                | uninodal   |
| BIZVEM[144] | ![Topology](image)     | \(\{4.6^2\}_2\{4.6.4.6\}\) | 3, 4-c | 2-nodal   |
| GIZSIS[145] | ![Topology](image)     | \(\{3^2.4\}_2\{3^3.4,3^2.4\}\) | 3,10-c | 2-nodal   |
| RANBAK[146] | ![Topology](image)     | \(\{3.4.5.6^2.7\}_2\{3.6.7\}_2\{3^2.4^2.5\}_2^2.6^2.7^4.8\}_*\) | 3,4,6-c | 3-nodal   |
| LILYIP[147] | ![Topology](image)     | \(\{3^2.4\}_2\{3^3.4,3^2.4\}\) | 3,10-c | 2-nodal   |
| (Considering an octacobalt cluster as a single node) | | | | |
| JOCGIS[148] | ![Topology](image)     | \(\{3.4.5.6^2.7\}_2\{3.6.7\}_2\{3^2.4^2.5\}_2^2.6^2.7^4.8\}_*\) | 3,4,6-c | 3-nodal   |
Table 1. Cont.

| Molecule | Topology | Coordination | Node Type |
|----------|----------|--------------|-----------|
| KOBHEP[40] | \{4^{3.6} \{4^4\} \{4^4\} \{4^2,6^2\}\} | 3,4,4,4-c | 4-nodal |
| KOBHAL[40] | \{3^{4.6}.6\{3^2,4^4\}\{3^2,4^4\}\{3^2,4.6^2\}\} | 3,4,5,5-c | 4-nodal |

* Symbols annotated with asterisk are point symbols (Schläfli symbol)

5. Three-Dimensional Coordination Frameworks

5.1. dia

dia is a most common 3-D uninodal topology with the point symbol of \{6^{6}\} (see dia in Figure 4). It contains one kind of 4-c node. All target structures with dia topology have an interpenetration style, which is caused by the large porous structure of a single dia framework. Rather than the three penetrated framework in AGOMOZ and SEYVIC, the four penetrated framework in LUMDEC, METYIU and NEHZIK, is preferred, which may stem from the presence of a slimmer ligand. In all the six dia structures (Figure 4), metal atoms are the 4-connected nodes and 2-connected ligands serve as edges.

AGOMOZ[149] SEYVIC[150] LUMDEC[150] LUMDIG[150] METYIU[151] NEHZIK[152]

5.2. sra

sra is a uninodal 4-connected topology with the point symbol of \{4^2,6^{3.8}\} (see sra in Figure 4). Four out of five of the sra structures consist of tetrazole-containing ligands. In all the result, both metal atoms and ligands serve as 4-connected nodes and few has coordinative water on metal atoms.

RAPBEP[153] GAMFEG[154] INOXUE[30] INOYAL[30] KOCWAB[41] QEYXAU[155]

5.3. etb

etb is a uninodal topology with one kind of 3-connected node and its point symbol is \{8^3\} and vertex symbol is [8.8.8(2)] (see etb in Figure 4). Both of the cadmium atoms and titled ligands in VERQOZ are 3-connected vertexes with terminal pyridines on the metal atoms.

VERQOZ[156]
Figure 4. Topology of the uninodal three-dimensional networks.

5.4. etc

etc is also a uninodal topology with one kind of 3-connected node and its point symbol is \( \{8^3\} \) and vertex symbol is \([8.8.8(2)]\) (see etc in Figure 4), which are same the etb, but they represent different topologies. Both of the manganese atoms and title ligands in WOMFIO are 3-connected vertexes leading to three-dimensional porous structure in which small solvent molecules are contained.

5.5. pcu

pcu (primitive cubic), another common topology, is a 6-connected uninodal net with the point symbol of \( \{4^{12}.6^3\} \) (see pcu in Figure 4). Oddly pcu is rare, with only one instance ODIVUT in which cobalt atoms serve as all 6-connected nodes while bridging title ligands and water serve as edges.

5.6. ths

Topology ths has the point symbol of \( \{10^3\} \) which is a uninodal net containing only 3-connected nodes (see ths in Figure 4). Both the ligands and metal atoms serve as the 3-connected nodes.
Figure 5. Topology of the binodal three-dimensional networks.

5.7. rtl

Topology rtl has the point symbol of \( \{4,6^2\}_2\{4^2,6^{10},8^3\} \). It contains 3-connected nodes and 6-connected nodes (see rtl in Figure 5). All rtl structures also use tetrazole-containing ligands as 3-connected nodes exclusively, and metal atoms as 6-connected nodes.

5.8. pts

Topology pts has the point symbol of \( \{4^2,8^4\} \) and vertex symbol of \([4.4.8(7).8(7).8(7).8(7)]\) \([4.4.8(2).8(2).8(8).8(8)]\) (see pts in Figure 5). The vertex symbol shows that there are two different 4-connected nodes in the framework. All pts structures have tetrazole-containing ligands since they have
enough coordination atoms to form the 4-connected nodes. Metal atoms form the other kind of 4-connected nodes.

5.9. ant

Topology ant contains 3-connected nodes and 6-connected nodes and has the point symbol of \( \{4^2.6\}_2 \{4^4.6^2.8^8.10\} \) (see ant in Figure 5). JOJJEY is the only entry that has the ant topology. Zinc atoms are its 6-connected nodes while title ligands are the 3-connected nodes.

5.10. bbf

There are two different kinds of 4-connected vertexes in topology bbf whose point symbol is \( \{6^4.8^2\}_2 \{6^6\} \) (see bbf in Figure 5). UHUNEQ, in which copper atoms and titled ligands represent different 4-connected nodes, is the only entry that possesses bbf topology.

5.11. dmc

3-connected nodes and 4-connected nodes are presents in dmc topology whose point symbol is \( \{4.8^2\}_2 \{4.8^3\} \) (see dmc in Figure 5). The only instance of dmc in this research is XOHPOA, whose 4-connected nodes are cadmium atoms and 3-connected nodes are title ligands. 2-connected pillars are also contained in the structure.

5.12. pyr

pyr is a 3,6-connected binodal net with point symbol of \( \{6^{12}.8^3\}_2 \{6^3\} \) (see pyr in Figure 5). QEYWUN is the only structure here that has a pyr topology. Cadmium atoms serve as 6-connected node and title ligands as 3-connected nodes.

5.13. sqc5577

sqc5577 is a 4,4-connected binodal net in epinet.ttd database in TTD collection with the point symbol of \( \{4^2.6^2.8^2\}_2 \{4^2.6^3.8\} \) (see sqc5577 in Figure 5). Both cadmium atoms and title ligands serve as 4-connected nodes of a different type.
5.14. stp

**stp** is a 4,6-connected binodal net with a point symbol of \( \{4^4.6^2\}_3\{4^9.6^6\}_2 \) (see **stp** in Figure 5). Both title ligands and carbonate ions in AGARUW are 4-connected nodes and the lanthanum atoms are 6-connected nodes. It is a porous structure.

5.15. tfz

**tfz** is a 3,4-connected binodal net. Its point symbol is \( \{6^3\}_2\{6^4.8.10\}_3 \) (see **tfz** in Figure 5). Like KAVGAQ, **tfz** is formed by connection of edge center of neighboring **hcb** layers, but has a higher symmetry.

In REJLOI, title ligands are the 3-connected nodes and cobalt atoms are the 4-connected nodes.

5.16. KAVGAQ

**KAVGAQ** is a unique topology only present in coordination polymers with an imidazole-4,5-dicarboxylic acid ligand. It can be recognized by the central points of edges of **hcb** layers connected by pillars (see **KAVGAQ** in Figure 6). Its point symbol is \( \{6^3\}_2\{6^4.10^2\}\{6^4.8^2\}_2 \). One kind of 3-connected node and three kinds of 4-connected node are present. In all instances, title ligands serve as 3-connected nodes and metal atoms as 4-connected nodes.

5.17. RAPBIT

**RAPBIT** is a unique 5, 6, 6-connected 3-nodal net whose point symbol is \( \{3.4^3.5^6.6^3\}_2\{3.4^6.5^3\}_2\{3^2.4^2.5^2.6^4.7^4.8\} \) (see **RAPBIT** in Figure 6). Cadmium atoms are separated into two classes of 6-connected nodes while title ligands are the 5-connected nodes.
5.18. New three-dimensional topologies

Twenty four new topologies which are not present in the TTD collection are listed below (Shown in Table 2).

Table 2. New Three-Dimensional Topologies.

| CSD Refcode   | Topology Demonstration | Point Symbol (Schläfli Symbol) | Nodal Connectivity | Node Types |
|---------------|------------------------|-------------------------------|-------------------|------------|
| UFETAB[143]   |                        | \{6^6\}                       | 4,4-c             | uninodal   |
| POLDOQ[129]   |                        | \{4^2.8^4\}                  | 4-c               | uninodal   |
| POLDUQ[129]   |                        | \{6^6\}                       | 4,4-c             | uninodal   |
| MOFTIL[46]    |                        | \{6^6\}                       | 4,4-c             | uninodal   |
| MOFTIL01[47]  |                        | \{4.8^2\} \{4.8^3\}         | 3,4-c             | binodal    |
| ACUXAY[166]   |                        | \{4.8^2\} \{4.8^3\}         | 3,4-c             | binodal    |
| Molecule     | Dimensions | Connectivity | Nodality |
|--------------|------------|--------------|----------|
| BOHVEA[44]   | 3.4-c      | 2-nodal      |
| BOHVIE[44]   | 4.82.10^3  | 3,4-c        |
| XECBOX[165]  | {10^3}     | 3,3-c        | uninodal |
| MEVBIZ[151]  | {4.6.8} {4.6^2.8.10^2} | 3,4-c | 2-nodal |
| PEXSOB[93]   | {4.6^2} {4.6^2.8^2} | 3,5-c | 2-nodal |
| PEXSOB01[167]|            |              |
| QEYWOH[155]  | {4^2.6}_2 {4^4.6^2.8^7.10^2} | 3,6-c | 2-nodal |
| Molecule   | Molecular Structure | Substructures                  | Symmetry | Node Type |
|------------|---------------------|--------------------------------|----------|-----------|
| YELYUK[92] | ![Structure](image1) | {4^2.8^4} {4^6.8^3} {4^8.6^2}_2 | 4,5,6-c  | 3-nodal   |
| GIDKOU[168]| ![Structure](image2) | {4^2.5^2.7^2.8^4} \{4^2.5^2.7^2\}_2 {4^2.8^4} | 4,4,4,5-c | 3-nodal   |
| UFARUP[169]| ![Structure](image3) | {4^2.5^2.7^2.8^4} \{4^2.5^2.7^2\}_2 {4^2.8^4} | 4,4,4,5,5-c | 3-nodal   |
| UFASAW[169]| ![Structure](image4) | {4.5.6^3.7}_4 {4.5^2.6^4.7^2}_2 {5^2.8^4} | 4,4,4,5,5-c | 3-nodal   |
| DIXVUC[39] | ![Structure](image5) | {4.8^2}_6 {4^1}{4^6.6^4}_3 {8^{12}.12^3} | 4,4,4,5,6-c | 4-nodal   |
| Molecule     | Structure | Symmetry | Nodes | Nodality |
|--------------|-----------|----------|-------|----------|
| CETGEO[170]  | ![Structure](image) | \{4.8^4.10\} \{4.9^2\} \{8.9^2\} \{9^3\} | 3,3,3,4-c | 4-nodal |
| KOCWEF[41]   | ![Structure](image) | \{3.4.6^2.7^2\} \{3.4^2.5^2.6^2.7^2\} \{3^2.4^2.5^2.6^2\} \{3^2.4^2.5^2.6^2.7^2\} | 4,4,5,5,5,6,6-c | 4-nodal |
| WIJDAV[171]  | ![Structure](image) | \{6.10^2\} \{6.8.10\} \{8.10^2\} | 3,3,3,3-c | 4-nodal |
| LIZWEX[49]   | ![Structure](image) | \{4.6.8^2.10^2\}_6 \{4^2.6\}_6 \{4^3\}_2 \{6^2.8^4\}_3 | 3,3,4,4-c | 4-nodal |
| XECBIR[165]  | ![Structure](image) | \{4.6^2.8^2.9\}_2 \{4.8^2\}_2 \{4^2.5^2.6^2.7^2\}_2 \{4^2.5^2.7^2\}_2 \{4^2.6.8^3\} | 3,4,4,4,5-c | 5-nodal |
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|-------------------|------|

Table 2. Cont.

| Compound | Equation | Crystallographic Data | Nodality |
|----------|----------|------------------------|----------|
| KOLWUE[172] | 4.62, 4.64, 8.4, 10, 4.64, 8, 4.82 | 3,3,3,4,5-c | 5-nodal |
| KEPMIB[173] | 4.68, 10, 4.68, 14, 6.8, 8, {4.3.8} | 3,3,4,4,6-c | 5-nodal |
| GIKBOS[174] | 4.6, 8, 4.2, 6, 8, 4.2, 6, 8, 4.2, 6, 8, 4.2, 6, 8 | 3,4,4,5,6-c | 5-nodal |
| YELYOE[92] | 4.5, 5, 6, 4, 7, 8, 4, 7, 5, 8, 4, 7, 5, 8, 4, 7, 5, 8 | 4,5,5,5,5-c | 5-nodal |
| NEVHEC[175] | 4.8, 4.8, 4.8, 4.8, 4.8, 4.8 | 3,4,4,5-c | 4-nodal |
6. Summary and Conclusions

This review shows that a number of coordination sites provided by the azole-containing carboxylic acid ligand are readily available to bind to metal ions as polydentate O and N donors and these multifunctional ligands can provide a variety of the topology patterns in the resulting infinite metal-organic coordination networks (MOCNs). The diverse coordination modes of diazole, triazole and tetrazole-containing carboxylic acids and the various topology patterns in the one, two, and three-dimensional metal-organic coordination polymers enrich the fields of research in the coordination and structural chemistry of these compounds, and contribute plentiful novel MOFs materials with better practical value as supporting carriers, in gas sorption and magnetic, optic or electronic applications.

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