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Review

Metal-organic molecular architectures with 2,2′-bipyridyl-like and carboxylate ligands

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Contents

1. Introduction 546
2. Molecular architectures assembled via coordination bonds 546
    2.1. 1D coordination polymers 547
    2.2. 2D coordination polymers 548
    2.3. 3D coordination polymers 549
3. Molecular architectures assembled via hydrogen bonds 551
    3.1. 1D, 2D, and 3D architectures based on 0D coordination compounds 551
    3.2. Double-strand helices, zippers, 2D and 3D architectures based on 1D coordination polymers 552
    3.3. 3D architectures based on 2D coordination networks 554
4. Molecular architectures assembled via π–π interactions 555
    4.1. 1D, 2D, and 3D architectures based on 0D coordination compounds 555
    4.2. Double-strand helices, zippers, 2D and 3D architectures based on 1D coordination polymers 557
    4.3. 3D architectures based on 2D coordination networks 562
5. Conclusions and outlook 564
Acknowledgements 564
References 564

Abstract

This review provides an overview on the crystal structures and properties of metal carboxylate coordination compounds with 2,2′-bipyridyl-like ligands reported in the past 4 years, which exhibit interesting structural features. This covers coordination polymers in one, two and three dimensions, as well as molecular architectures assembled by hydrogen-bonding and/or π–π stacking interactions from low-dimensional entities to higher-dimensional supramolecular architectures.

Keywords: Molecular architecture; Supramolecular interactions; Coordination bond; Hydrogen bond; π–π; Interactions; 2,2′-Bipyridine; 1,10-Phenanthroline; Carboxylate

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Abbreviations: bpy, 2,2′-bipyridine; dmbpy, 4,4′-dimethyl-2,2′-bipyridine; dmphen, 2,9-dimethyl-1,10-phenanthroline; Hglyo, glycolic acid; Hobpy, 6-hydroxy-2,2′-bipyridine; Hophen, 2-hydroxy-1,10-phenanthroline; 3-Hpya, *trans*-3-(3-pyridyl)acrylic acid; 4-Hpya, 4-pyridylacrilic acid; Hsba, 4-sulfobenzoic acid; Hsbal, *N*-(2-hydroxybenzyl)-β-Alanine; Hsgly, (*N*-(2-hydroxybenzyl)-α-glycine; Hsval, (*N*-(2-hydroxybenzyl)-α-valine; H_2aa, adipic acid; 1,2-H_2bdc, 1,2-benzenedicarboxylic acid; 1,3-H_2bdc, 1,3-benzenedicarboxylic acid; 1,4-H_2bdc, 1,4-benzenedicarboxylic acid; H_2bpa, 4,4′-biphenyldicarboxylic acid; 3,3′-H_2bpyda, 2,2′-bipyridyl-3,3′-dicarboxylic acid; 4,4′-H_2bpyda, 2,2′-bipyridyl-4,4′-dicarboxylic acid; H_2chdc, 1,4-cyclohexanedicarboxylic acid; H_2eob, ethylenedi(4-oxybenzenecarboxylic acid); H_2fum, fumaric acid; H_2glu, glutaric acid; H_2ma, maleic acid; H_2oba, 4,4′-oxybis(benzenecarboxylic acid); H_2pa, pimelic acid; H_2sal, salicylic acid; H_2sala, (*N*-(2-hydroxybenzyl)-α-alanine; H_2su, succinic acid; H_2sub, suberic acid; H_2tda, thiodiglycolic acid; H_3bta, 1,2,4-benzenetricarboxylic acid; H_3btc, 1,3,5-benzenetricarboxylic acid; H_3nat, nitrilotriacetic acid; H_3oa, orotic acid; 4-H_3oip, 4-hydroxyisophthalic acid; 5-H_3oip, 5-hydroxyisophthalic acid; H_3sip, 5-sulfoisophthalic acid; H_4btac, 1,2,4,5-benzenetetracarboxylic acid; mal, malonate dianion; ox, oxalate dianion; phen, 1,10-phenanthroline

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1. Introduction

Crystal engineering of metal complexes, especially coordination polymers has been greatly developed in the past decade [1–8]. Coordination molecular architectures consist of metal ions (and metal clusters) functioning as nodes and organic ligands as bridges. These exhibit a wide range of infinite zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D) frameworks with different interesting structural features, resulting from coordination bonding, hydrogen bonding, aromatic π–π stacking interactions as well as van der Waals forces [1–8]. Aside from coordination bonding interactions, relatively strong hydrogen bonding and π−π stacking interactions, the solvent molecules, counterions and templates also influence the formation of the ultimate architectures. As such, non-coordinating ions or molecules may sometimes be used to control the crystallization processes and solid-state architectures. On the other hand, many supramolecular architectures based on metal–ligand interactions have, in fact, been designed for purely symmetry and esthetics grounds. The intense interest in this field, given impetus by synthetic and theoretical chemists, crystallographers and materials scientists, has resulted not only in beautiful and diversified structures, but in potential applications as electronic, magnetic, optical, absorbent and catalytic materials [7,9].

Coordination molecular architectures can be directly constructed by coordination bonds using metal ions existing in varied coordination geometries (for example, tetrahedron, square, trigonal bipyramid or octahedron) to combine with multifunctional (linear or angular bidentate, planar or pyramidal tridentate, planar or tetrahedral quadridentate) ligands into multi-dimensional frameworks. Another synthetic approach utilizes supramolecular synthons since π–π stacking interactions and hydrogen bonds have directionality and recognition compared with weak electrostatic interactions and van der Waals forces [10]. The strengths of these interactions are moderate, falling between the extremes of strong covalent bonds and weak van der Waals forces. Compared with inorganic compounds, however, coordination polymers built upon molecular building-blocks hold great promise for processability, flexibility, structural diversity, and geometrical (size, shape, and symmetry) control. As such, supramolecular architectures assembled by coordination bonds and/or supramolecular interactions allow for more predictable control over directional assemblies and packing arrangements in the solid state.

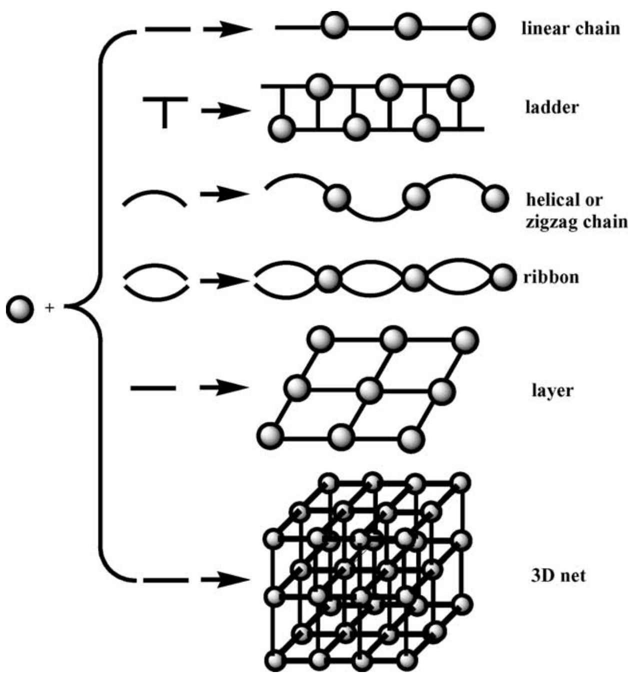
The exo-bidentate dipyridyl heterocyclic compounds as bridging ligands, include, for example, 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethane and *trans*-bis(4-pyridyl)ethene; the chemistry of coordination polymers of these ligands has recently been reviewed [11,12]. In contrast to the exo-bidentate dipyridyl compounds, 2,2′-bipyridyl-like (designated as bpy-like hereafter) ligands are bidentate chelating ligands, which can only act as terminal ligands and may provide supramolecular interaction sites for molecular recognition. Meanwhile, as bridging ligands, carboxylates, especially multi-carboxylates are of immense interest in the construction of polymeric coordination architectures owing to the fact that these polymers have a wide range of structural diversities and potential applications as porous materials and magnetic materials [7,9].

We have been interested in this aspect of coordination polymers, but we have not found any recent critical review of this subject, particularly from the crystallographic view. In this review, we summarize the recent progress in design and crystal structural investigations of coordination supramolecular networks based on bpy-like (such as bpy, phen and their derivatives) and carboxylate ligands, which are assembled by coordination bonds, hydrogen bonds as well as π–π stacking interactions. The literature covers the years 2000–2003, along with some reports which appeared in January 2004. The coordination-bonded frameworks are categorized into 1D, 2D and 3D polymeric architectures in Section 2, in which the supramolecular hydrogen bonding and π−π interactions do not play a critical role; the supramolecular architectures assembled via hydrogen bonds and π−π interactions based on the low-dimensional metal complexes are presented in Sections 3 and 4, respectively.

2. Molecular architectures assembled via coordination bonds

One of the most challenging research fields in modern chemistry is the design and synthesis of multifunctional compounds and materials with predictable structures and properties. In the 1970s, A.F. Wells focused on the overall structures of inorganic compounds and abstracted crystal structures in terms of their topology by reducing them to a series of points of a certain geometry that are linked to a fixed number of other points [13]. The final structures can thus be described either as polyhedra or as infinite networks. In the early 1990s, R. Robson developed and extrapolated Wells' work into the realm of metal-organic compounds and coordination supramolecular chemistry [14].

In order to design the targets with the different structural features and potential functions, an important step is selection and synthesis of the nodes including mono-, bi- and poly-nuclear structural units. Different metal ions may exhibit different coordination geometries. For example, two- or three-coordinate motifs with linear or T-shaped fashions found in Ag(I) and Cu(I) complexes can be employed to assemble a large number of supramolecular architectures [15] (Scheme 1). Square-planar and tetrahedral coordination motifs, are usually found in four-coordinate metal complexes, and have been well documented in supramolecular architectures [3,16]. Octahedral coordination spheres are ubiquitously adopted to construct coordination polymers. Metal ions in different coordination geometries as



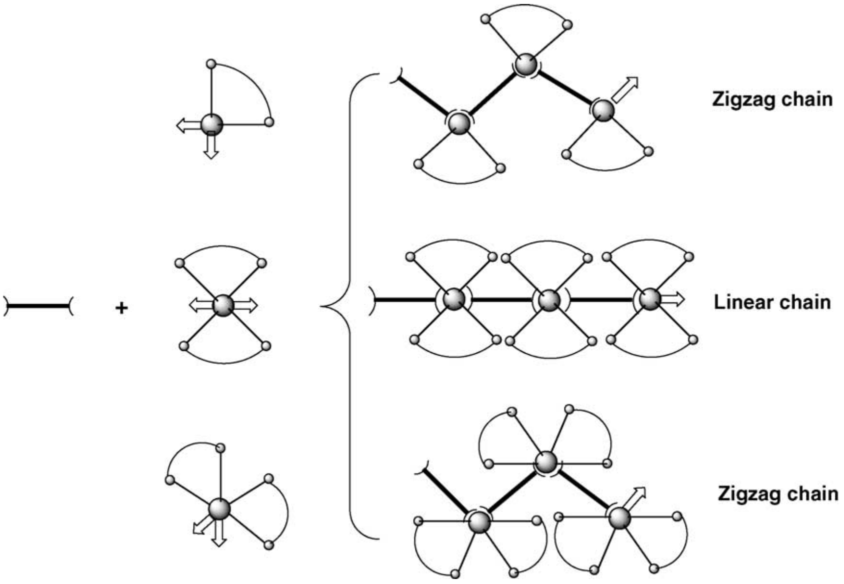
Scheme 1. Topologies of some coordination polymers.

well as metal clusters can then be connected by a large number of bridging ligands via coordination bonds into multi-dimensional frameworks [2–8,15,16].

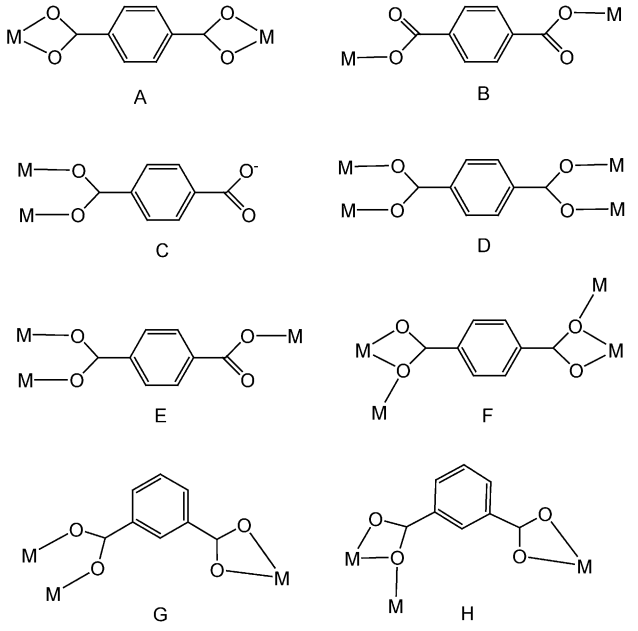
As bridging ligands, monocarboyxlates and polycarboxylates play an important role in the construction of coordination polymers (Scheme 1). Even in the co-existence of chelating bpy-like ligands, carboxylates can also connect metal ions or metal clusters into coordination polymers exhibiting intriguing structural and dimensional diversities.

2.1. 1D coordination polymers

The presence of the bpy-like ligands lowers the tendency of metal complexes to form high-dimensional carboxylate-bridged metal complexes with mononuclear metal ions as nodes, as many metal ions have coordination numbers of six or even less. For example, the assembly of two-coordinate, *trans*-four-coordinate, *trans*-five-coordinate and *trans*-six-coordinate metal ions with mono- and di-carboxylate as bridging ligands in the presence of bpy-like compounds as terminal ligands readily furnishes linear coordination polymers; for *cis*-four-coordinate and *cis*-five-coordinate as well as *cis*-six-coordinate metal ions, zigzag or helical coordination chains are formed (Scheme 2). For example, the hydrothermal reaction of $Cd(OH)_2$ with Hsa and bpy yielded $[Cd_2(sa)_2(bpy)_2(H_2O)_2]$, in which the $[Cd_2(sa)_2(bpy)_2(H_2O)_2]$ units are linked together by μ-carboxylate groups resulting in the formation of a 1D coordination polymer, which exhibits blue fluorescence [17]. Hydroxyl carboxylate ligands were also used in the synthesis of the isomorphous 1D polymers $[Cu(glyo)_x(ox)_{1-x}(bpy)]\cdot 2.5H_2O$ (x = 0.44 and 0.291). Each consists of alternate rhombic bis(μ-hydroxy)-bridged Cu(II) dimers [Cu···Cu distance 3.282(1) Å] and bis(μ-carboxylate)-bridged Cu(II) dimers [Cu···Cu distance 5.237(1) Å] [18]. The reaction of salicylaldehyde with β-alanine followed by reduction of the C=N bond in the product gave the multidentate ligand sbal; the 1D copper polymer $[Cu_3(sbal)_2(phen)(H_2O)_2](ClO_4)_2\cdot 3H_2O$ has both $[Cu_2(sbal)_2(H_2O)_2]$ and $[Cu(phen)]^{2+}$ entities as building blocks [19]. The two Cu(II) ions in the dimer have distorted square-pyramidal geometries composed of two tridentate dianionic sbal ligands with bridging phenolate groups. Additionally, the two carbonyl groups of the sbal ligands link the $[Cu(phen)]^{2+}$ fragments so that a 1D polymer results. A



Scheme 2. Different 1D polymeric structures.



Scheme 3. Coordination modes of some dicarboxylate groups.

similar complex, $[Cu_2(phen)(sal)(Hsal)_2]$, that is bridged by sal ligands into a 1D coordination polymer, is also known [20]. Complex $[Cu(Hsala)(phen)](ClO_4)\cdot 0.625H_2O$ is a helical coordination polymer having *anti–anti* carboxylate groups between adjacent Cu(II) ions and the asymmetric units are related by a crystallographic 2_1-screw axis [21].

Poly-carboxylates are widely used in the assembly of supramolecular architectures because of their diverse coordination modes and bridging ability. Among them, the best studied are the dicarboxylates and tricarboxylates. For example, the 1,4-bdc ligand can function in chelating bis-bidentate (a), bis-monodentate (b), mono-bidentate (*syn–syn*) (c), bridging bis-bidentate (d), monodentate–bidentate (e) or chelating/bridging bis-bidentate (f) modes, as shown in Scheme 3.

The reactions of 1,4-dicyanobenzene, phen and metal (Co, Zn or Cu) salts under hydrothermal conditions yield the polymeric complexes $[M(1,4\text{-bdc})(phen)(H_2O)]$ (M = Co and Zn) and $[Cu(1,4\text{-bdc})(phen)]$ [22]. Obviously, the cyano groups are converted into carboxylate groups under these conditions. The complexes adopt zigzag chain structures bridged by the 1,4-bdc ligands in the bis-monodentate fashion. The chain in $[Zn(bpy)(1,2\text{-bdc})(H_2O)]$ is a single-strand helix in which each zinc ion is six-coordinated by two nitrogen atoms from a bpy, one aqua oxygen atom, two oxygen atoms from one 1,2-bdc and one oxygen atom from another 1,2-bdc; effectively, each 1,2-bdc serves as a bridge between two zinc ions [23].

Aside from the aromatic dicarboxylates, a number of 1D coordination polymers bridged by alkyl dicarboxylates have also been structurally characterized. In $[Cu_2(fum)(\mu\text{-OH})(bpy)_2(H_2O)](NO_3)\cdot 2H_2O$, the polymeric chain is made up of dinuclear $[Cu_2(\mu\text{-OH})(bpy)_2]^{3+}$ units which are further linked together by the fum anions [24]; in $[Cu_4(Hsm)_5(dmbpy)_4](ClO_4)_3\cdot H_2O\cdot 0.53MeOH$, the polymeric chain consists of $[Cu_2(Hsm)_2(dmbpy)_2]^{2+}$ and $[Cu_2(Hsm)_3(dmbpy)_2]^{+}$ units that are further connected by the Hsm carboxylate [25].

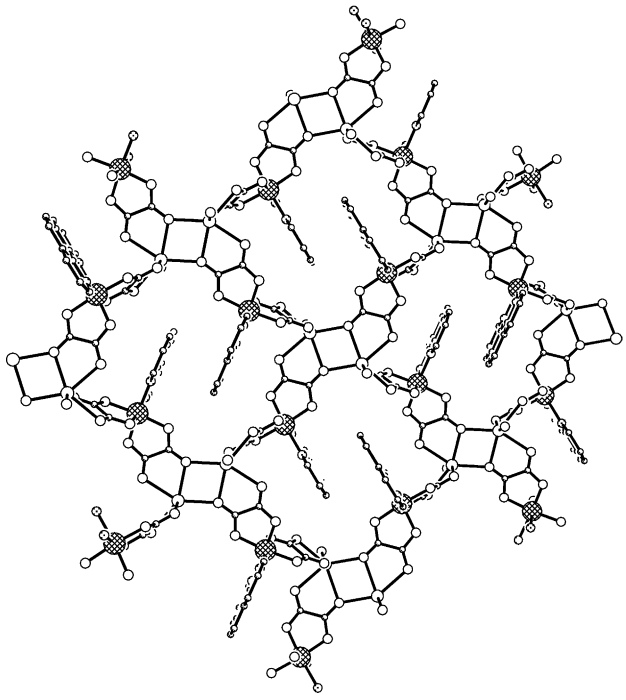


Fig. 1. The 2D (4,4) net of $[NaCr(phen)(ox)_2(H_2O)]\cdot 2H_2O$ (adapted from Ref. [26]).

2.2. 2D coordination polymers

The oxalate ligand is the simplest dicarboxylate. The ox-bridged heterobinuclear complex, $[NaCr(phen)(ox)_2(H_2O)]\cdot 2H_2O$ [26], displays a (4,4) 2D square network, in which each square unit is made up of four Na^+ dimers at the corners and four Cr^{3+} ions at the midpoint of the edges (Fig. 1). Magnetic studies suggested very weak antiferromagnetic interactions between the Cr(III) ions in this mixed-metal complex. In the dinuclear complex $[Eu(1,2\text{-bdc})(1,2\text{-Hbdc})(phen)(H_2O)]_2$, each Eu(III) ion is eight-coordinate; it is surrounded by three oxygen atoms from three 1,2-bdc anions, two oxygen atoms from two Hbdc anions, one oxygen atom from an aqua ligand, and two nitrogen atoms from one chelating phen molecule [27]. The Eu(III) ions in the dimer are bridged by carboxylate groups from 1,2-Hbdc and 1,2-bdc anions at a distance of 4.159 Å (Fig. 2). Interestingly, the dimeric units are further connected by the 1,2-bdc ligand into a 2D herringbone architecture having a Z-shaped mosaic.

The 2,2′-bipyridine dicarboxylates, such as 4,4′-bpyda and 3,3′-bpyda, are a special class of bridging multidentate ligands possessing both bpy and carboxylate groups. The hydrothermal reactions of the divalent metal salt with 4,4′-bpyda yield $[M(4,4'\text{-bpyda})(H_2O)]\cdot H_2O$ (M = Fe, Co, Ni

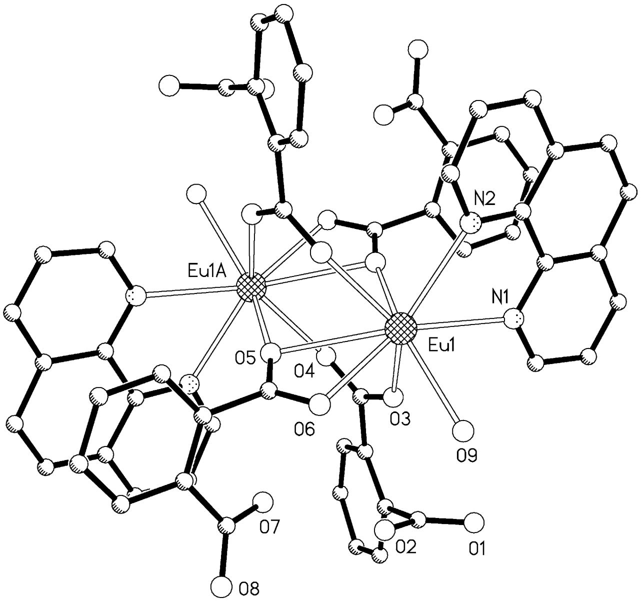


Fig. 2. The coordination environments of the Eu(II) ions in [Eu(1,2-bdc)(1,2-Hbdc)(phen)(H_2O)]$_2$ (adapted from Ref. [27a]).

and Zn) [28]. They are isomorphous and exhibit 2D network structures, constructed from six-coordinate M(II) sites linked through the 4,4′-bpyda ligands, each of which serves to bridge three metal sites. The lattice water molecules occupy cavities within the layers and are hydrogen bonded to the pendant carboxylate oxygen atom. Coordination polymers of 3,3′-bpyda will be described in Sections 3.2 and 4.2.

2.3. 3D coordination polymers

Three-dimensional coordination polymers provide an opportunity for making open framework compounds with controllable channel and cavity sizes, i.e., they are potentially porous compounds that are able to host inorganic ions or organic molecules. Unfortunately, owing to the termination effect of chelating bpy-like ligands, such coordination polymers containing both poly-carboxylates and bpy-like ligands are usually only 1D and 2D coordination polymers, such as those described in the previous and following sections. One strategy to increase the dimensionality of the coordination polymers makes use of di- or poly-nuclear secondary building blocks or nodes as these can provide more coordination sites and hence increase the possible formation of 3D coordination polymers. For example, when a dicarboxylate, such as 1,4-bdc, is employed, a polymeric chain with dinuclear unit [M_2(dicarboxylate)$_4L_2$] (L = bpy-like ligand) can be produced [22], in which the two metal ions can be linked by two carboxylate ends of the dicarboxylate ligands. Such chains can further be extended into the final 3D architecture, as exemplified by a complex [Mn(1,4-bdc)(phen)], which possesses a dinuclear [Mn_2(phen)$_2$(1,4-bdc)$_4$] building block bridged by two μ-carboxylate ends with the Mn. . .Mn distance of 4.810(2) Å, as shown in Fig. 3 [22]. The Mn(II) ion is coordinated by two nitrogen atoms from phen and four oxygen atoms from different 1,4-bdc ligands in a distorted octahedron geometry. Each 1,4-bdc ligand adopts a μ_4-bridging mode linking four Mn(II) ions, and each Mn(II) is attached to four 1,4-bdc ligands into 3D network with rhombus channels as shown in Fig. 4.

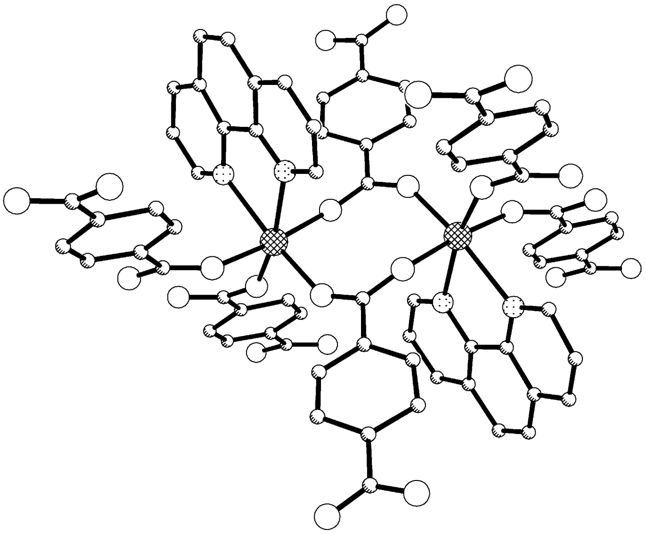


Fig. 3. The coordination environments of the Mn(II) ions in [Mn(phen)(1,4-bdc)] (adapted from Ref. [22]).

When a carboxylate bridge in the above example is replaced by a chloride ion, the resulting μ-Cl bridged chains can also be connected into a 3D network through the μ_4-bridging 1,4-bdc ligands. In [Cd(1,4-bdc)$_{0.5}$(phen)Cl], each Cd(II) ion lies in a distorted octahedron completed by two nitrogen atoms from a phen, two chloride ions and two carboxylate oxygen atoms [22]. The 1,4-bdc ligand also adopts a μ_4-bridging mode, linking four Cd(II) ions. A pair of Cd(II) ions are bridged by two μ-Cl groups into a dimer at a distance of 3.940(1) Å, and the dimers are interconnected in a head-to-tail fashion by a carboxylate bridge into polymeric chains. The chains are further connected by the μ_4-1,4-bdc ligand into the 3D structure in the lattice [22].

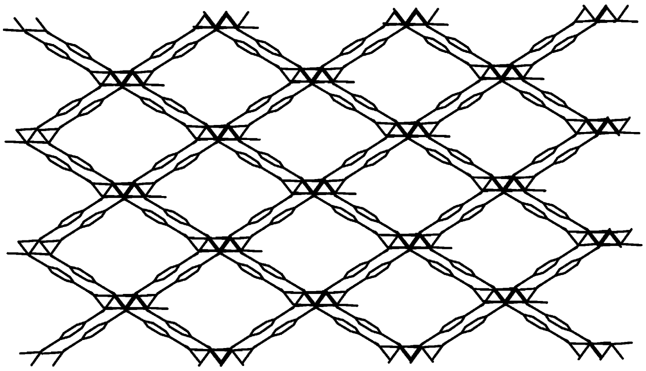


Fig. 4. Molecular packing of [Mn_2(phen)$_2$(1,4-bdc)$_4$] (the atoms of phen are omitted) (adapted from Ref. [22]).

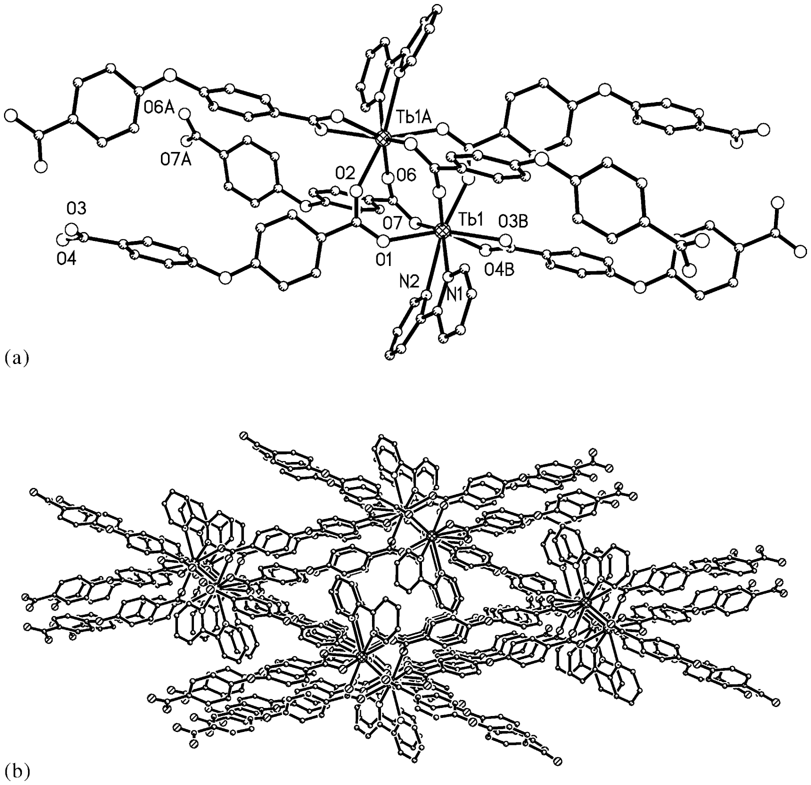
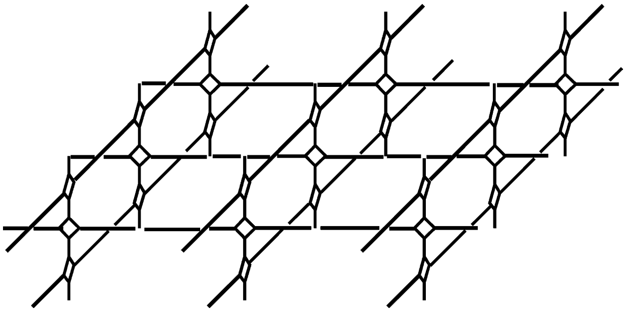


Fig. 5. Perspective views of (a) the coordination environment of the dimeric center and (b) 3D network in $[Tb_2(oba)_3(bpy)_2]$ (adapted from Ref. [29]).

Another strategy to increase the coordination dimensionality in the presence of the chelating bpy-like ligands is the use of metal ions of higher coordination numbers such as lanthanide(III) ions [designated as Ln(III)], and a number of examples have been documented in these Ln(III) dicarboxylates. When the high-coordinate Ln(III) ions were employed to react with dicarboxylate ligands in the presence of bpy, two isostructural complexes $[Ln_2(oba)_3(bpy)_2]$ (Ln = Tb and Er) were obtained [29,30], in which each Ln(III) ion is eight-coordinated by four oxygen atoms from four bidentate bridging oba ligands, two oxygen atoms from a chelate carboxylate end of oba, as well as two nitrogen atoms from a chelate bpy, as shown in Fig. 5a. Two pairs of oba ligands in a dimeric unit are connected to two adjacent dimeric units in the chelating–bridging bidentate fashion to give rise to a polymeric chain. These chains are cross-linked by oba ligands in the bridging bis-bidentate fashion into a 3D framework featuring a rhombic net motif, as shown in Fig. 5b and Scheme 4; the bpy ligands reside within the rhombic "channel" and are chelated to the metal ions. The $[Eu_2(1,3\text{-bdc})_3(phen)_2(H_2O)_2]\cdot 4H_2O$ displays two types of rings: one is an eight-membered ring composed of two carboxylate groups and two Eu(III) ions whereas the other is a 32-membered ring formed by four 1,3-bdc groups bridging four Eu(III) ions [27a]. The 1,3-bdc ligands are coordinated to Eu(III) ions through three oxygen ions of the carboxylate groups to lead to a 2D network structure (Fig. 6). The layers intersect at the Eu(III) ions to form a 3D network. Similar 3D network patterns are also observed in $[Yb_2(1,3\text{-bdc})_3(phen)_{0.5}]$, $[Tb_4(1,3\text{-bdc})_6(phen)]$ and $[Er_4(1,3\text{-bdc})_6(phen)]$ [27]. The btc tricarboxylate is a multidentate ligand and has also been used in the assembly of porous, zeolite-like 3D frameworks [31]; in the presence of phen, $[Mn_3(btc)_2(phen)_3]$ was obtained by the hydrothermal reaction of H_3bdc and manganese acetate [32]; the complex exhibits a 3D network structure.

Aside from the construction of 2D coordination network (see Section 2.2), 4,4′-bpyda can also furnish 3D microporous coordination polymers. The Mn(II) complex, $[Mn(4,4'\text{-bpyda})(H_2O)_2]$, synthesized hydrothermally from $Mn(NO_3)_2$ and $4,4'\text{-}H_2bpyda$ in aqueous ethanol [33], consists of bis(μ-carboxylate)-bridged dinuclear units having



Scheme 4. The 3D topologic network in $[Tb_2(oba)_3(bpy)_2]$. The small squares represent the dimeric units while the bars represent the dicarboxylates.

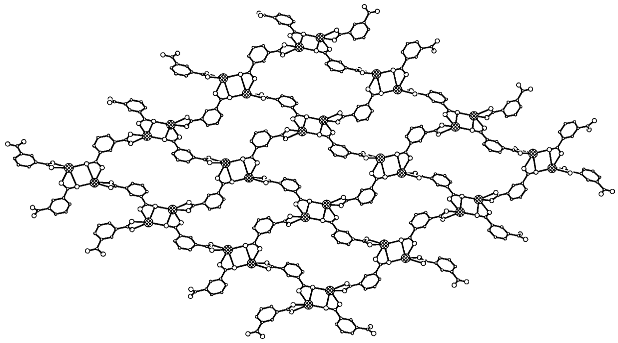


Fig. 6. 2D network of $[Eu_2(1,3\text{-bdc})_3(phen)_2(H_2O)_2]\cdot 4H_2O$. Other 1,3-bdc anions, phen ligand and hydrogen atoms are omitted for clarity (adapted from Ref. [27a]).

a Mn. . .Mn interaction of 2.73 Å; these are cross-linked via bis(carboxylate)-bridges into a 3D network. The resulting architecture exhibits channels having a pore size of 6.87 Å × 5.86 Å (Fig. 7). Analogous 3D coordination polymers, such as $[Tb_2(4,4'\text{-bpyda})_3(H_2O)_3]\cdot H_2O$ and $[Co(4,4'\text{-bpyda})(H_2O)_2]$ have also been observed [34].

3. Molecular architectures assembled via hydrogen bonds

The strength of multiple hydrogen bonds is roughly comparable with that of a metal–ligand coordination bond; as these possess the capability of molecular recognition and directionality, they have been exploited in supramolecular chemistry and crystal engineering. This subject, supramolecular architectures assembled mainly by hydrogen bonds, has been reviewed [11a,35–38]. In the context of hydrogen-bonded supramolecular architectures based on bpy-like and carboxylate ligands, the carboxylates themselves are a particular type of multi-functional unit. Not only can they bind to metal ions to form coordination polymers but they are also capable of functioning as hydrogen bond donors and/or acceptors. A large number of recent examples demonstrate an important and interesting role for such ligands in the supramolecular architectures based on the bpy-like and carboxylate ligands.

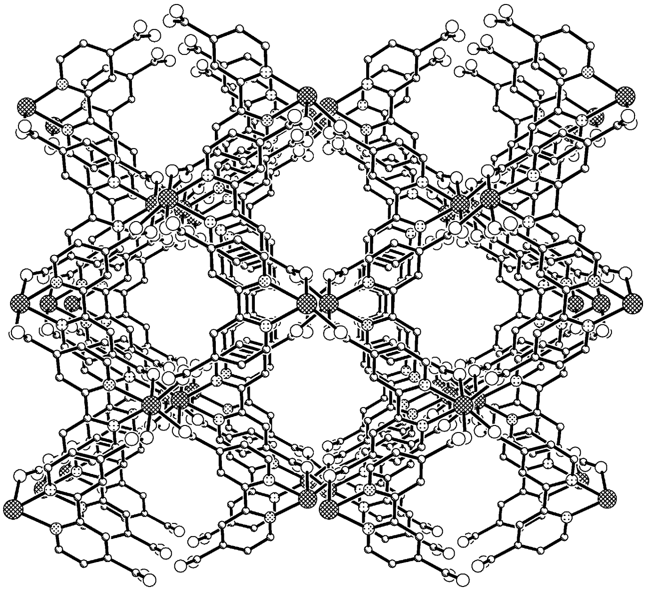


Fig. 7. Crystal structure of $[Mn(4,4'\text{-bpyda})(H_2O)_2]$ (adapted from Ref. [33]).

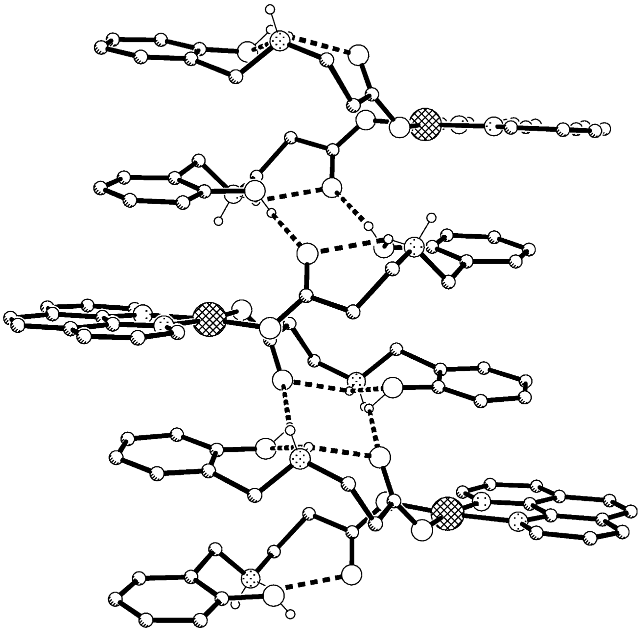


Fig. 8. The hydrogen-bonded spiral chain structure of $[Cu(H_2sbal)_2(phen)](ClO_4)_2$.

3.1. 1D, 2D, and 3D architectures based on 0D coordination compounds

In the presence of intermolecular hydrogen bonding interactions, 0D metal carboxylates can be readily assembled into high-dimensional supramolecular architectures via hydrogen bonds that involve the carboxylate groups, ligands with hydrogen-donor groups and solvent molecules. For example, in $[Cu(H_2sbal)_2(phen)](ClO_4)_2$, the carboxylic group of H_2sbal is deprotonated while the amine group is protonated, so that the H_2sbal ligand exists in a zwitterionic form [19]. As shown in Fig. 8, the Cu(II) ion is four-coordinate with the two nitrogen atoms form a phen and two carboxylate oxygen atoms from two H_2sbal ligands, the protonated amine group donates one hydrogen atom to the two oxygen atoms each from the phenolic and carboxylate groups, forming an intramolecular, tricentered hydrogen bond. Additionally, the phenolic protons interact with the carbonyl groups of the carboxylates in neighboring cations to generate a helical chain structure. At higher pH, the H_2Sbal ligand is deprotonated, and the synthesis yields the 1D coordination polymer, $[Cu_3(sbal)_2(phen)(H_2O)_2](ClO_4)_2\cdot 3H_2O$

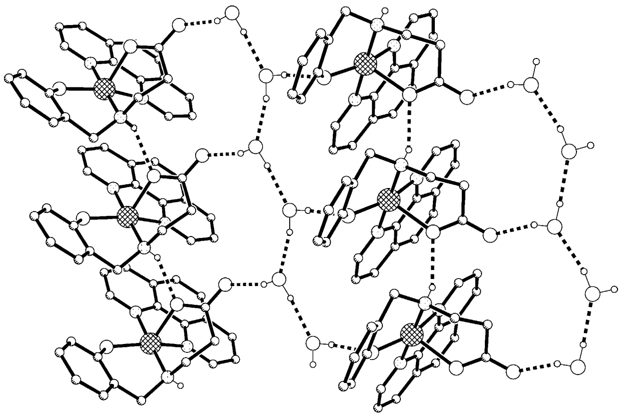


Fig. 9. The hydrogen-bonded 2D sheet in [Cu(sbal)(phen)]·H_2O.

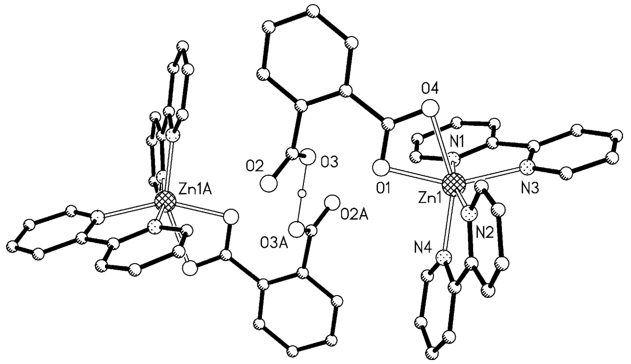


Fig. 10. Perspective view of the coordination environment of the zinc dimer linked by hydrogen bond in [Zn_2(bpy)$_4$(1,2-bdc)(1,2-Hbdc)](1,2-Hbdc)(1,2-H_2bdc)·2H_2O (adapted from Ref. [42]).

(which has been described in Section 2.1). In high pH media, [Cu(H_2sbal)$_2$(phen)](ClO_4)$_2$ and [Cu_3(sbal)$_2$(phen)(H_2O)$_2$] (ClO_4)$_2$·3H_2O are converted to a neutral monomer [Cu(sbal)(phen)] [19]. The two complexes, [Cu(sgly)(phen)]·2.75H_2O and [Cu(Hsgly)(phen)](ClO_4)·1.5H_2O, in which sgly is derived from glycine [21], are both 1D hydrogen-bonded polymers. Crystallographic analyses show these two Cu(II) complexes to be 1D hydrogen-bonded polymers. In [Ni(Hoa)(dmphen)(H_2O)], the Ni(II) ion is five-coordinated with the two nitrogen atoms from a dmphen, one water molecule, and one nitrogen atom and one oxygen atom from carboxylate of one oa ligand [39]. The aqua ligand donates a hydrogen bond to a carboxylate oxygen of an adjacent molecule to give rise to a hydrogen-bonded polymeric chain. On the other hand, the complex [Mn_2(mal)(phen)$_3$(H_2O)$_2$Cl]Cl comprises a dinuclear cation that is bridged by a single *anti–anti* malonate ligand [40]; each dimer links two neighboring ones via hydrogen bonding interactions between the aqua ligand, chloride ion and the oxygen atom of the mal ligand into a supramolecular chain.

In [Cu(sbal)(phen)]·H_2O, the amine proton of sbal is donated to a carboxylate oxygen atom of an adjacent molecule to generate a hydrogen-bonded chain [20]. Each lattice water molecule is strongly hydrogen-bonded to two other lattice water molecules and sbal carboxylate oxygen atom to give rise to a 2D sheet, as shown in Fig. 9. In mononuclear [Mn(mal)(bpy)(H_2O)$_2$], each monomeric entity is linked to six neighboring ones via hydrogen bonds between the aqua and mal ligands to give infinite supramolecular sheets [40]. Similarly, in [Zn(phen)$_2$(Hsub)](NO_3)·H_2O, the monomeric cations are also interconnected into 2D layers via hydrogen bonds between the non-coordinating carbonyl groups, nitrate groups and lattice water molecules [41].

Complex [Zn_2(bpy)$_4$(1,2-bdc)(1,2-Hbdc)](1,2-Hbdc)–(1,2-H_2bdc)·2H_2O features a hydrogen-bonded dinuclear building block, in which each Zn(II) ion is six-coordinated by four nitrogen atoms from two chelate bpy and two oxygen atoms from a chelate carboxylate group (Fig. 10) [42]; the hydrogen bond [2.459(3) Å] between a pair of the non-coordinating carboxylate groups from the two monomeric complexes is regarded as being very strong. The hydrogen-bonded dimers are further assembled via hydrogen bonds involving the lattice water molecules, free 1,2-bdc anions and neutral 1,2-H_2bdc molecules into a 3D polymeric network. The reaction of Zn(II) ions with H_2sub and phen in aqueous methanol gave two mixed-ligand Zn(II) complexes, [Zn_2(phen)$_2$(H_2O)$_2$(sub)$_2$]·5H_2O and Zn(phen)(Hsub)$_2$ [41], both of which adopt 3D open framework structures that are assembled via hydrogen bonds.

3.2. Double-strand helices, zippers, 2D and 3D architectures based on 1D coordination polymers

As multidentate ligands, carboxylates can bridge metal ions into coordination polymeric structures. When supramolecular interactions are permitted, lower-dimensional metal complexes and coordination polymers can be further assembled into molecular architectures of higher dimensionality. In this section, we will show that the 1D coordination polymers can be assembled into double-strand chains, 2D or 3D networks via hydrogen bonds. Complex [Mn(fum)(bpy)(H_2O)] consists of zigzag polymeric chains connected by the flexible dicarboxylate fum ligands, in which each Mn(II) ion is seven-coordinated by a chelate bpy, two bidentate carboxylates and one aqua molecule [43]. A pair of chains are linked into a double chains by hydrogen bonds involving the aqua ligand on one chain and two oxygen atoms of the fum ligand in the other chain as depicted in Fig. 11. Complex [Co(oba)(phen)(H_2O)] is an example of a neutral double-strand helix [44]; the V-shaped oba ligand acts as a bridge to connect two adjacent Co(II) ions (Fig. 12a). The helical nature is attributed to the V-shaped configuration of the bridging dicarboxylate ligand. The two adjacent chains interact through hydrogen bonds between the non-coordinating carboxylate oxygen atoms and the aqua ligand [O(2w)···O(1a) = 2.745(6) Å] to generate a double-strand chain, as shown in Fig. 12b. The phen ligands are attached to one side of the double-strand chain. Additionally, supramolecular interactions of strong aromatic π–π stacking between the phen ligands

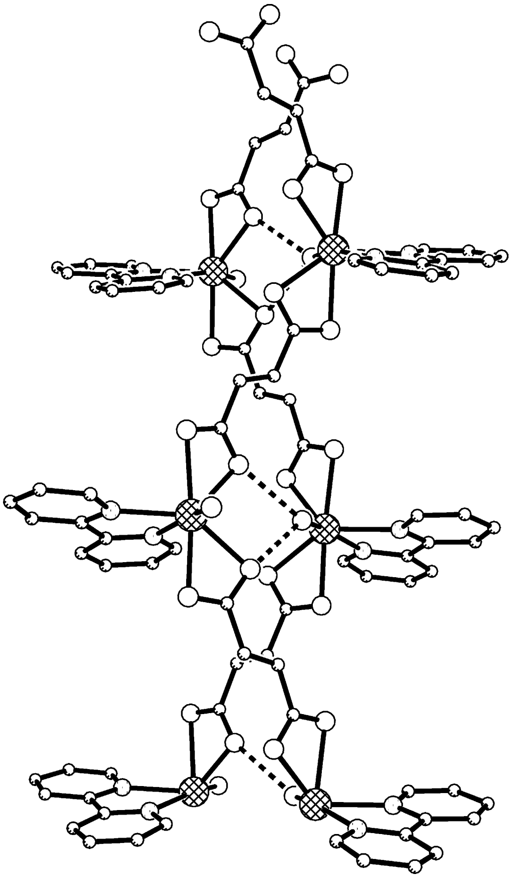


Fig. 11. Hydrogen bonded double-strand chains in [Mn(fum)(bpy)(H_2O)].

(face-to-face distance 3.48 Å) and hydrogen bonds between the aqua molecules [O(1w)···O(1wa) = 2.871(6) Å] from two adjacent chains further extend the double-strand chains into layers. Helical, multinuclear assemblies mediated by metal–ligand coordination are well documented in the literature [45,46]; a number of helical assemblies of purely organic molecules organized by hydrogen bonds [47,48] have also been described recently. However, hydrogen-bonded double-strand and triple-strand helical coordination polymers were not known.

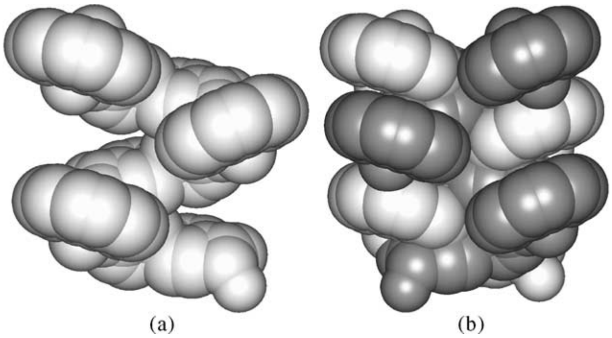


Fig. 12. Perspective views of the single-strand helical chain (a); double-strand chains generated by hydrogen bonds between two single-strand helical chains (b) in [Co(oba)(phen)(H_2O)] (adapted from Ref. [44]).

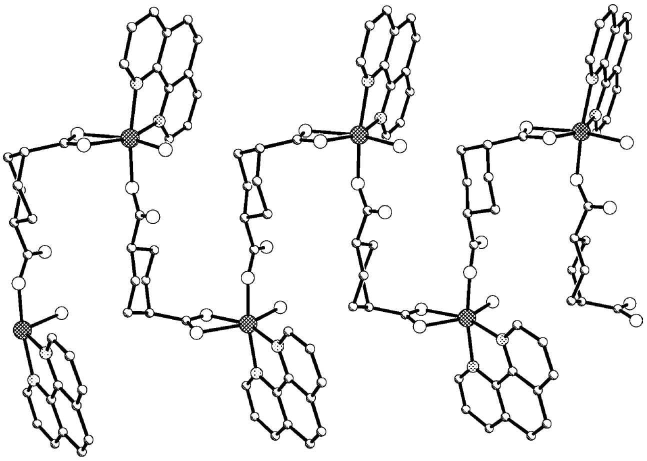


Fig. 13. The helical chain in [Co_2(phen)$_4$(chdc)$_2$(H_2O)$_2$].

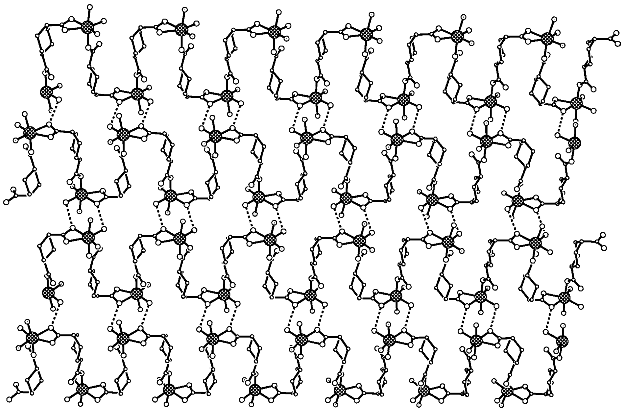


Fig. 14. The hydrogen-bonded alternative right- and left-handed helices. The carbon atoms of the phen ligands are omitted for clarity (adapted from Ref. [49]).

The dicarboxylate of a cyclic compound, 1,4-cyclohexanedicarboxylic acid (H_2chdc), was used in the synthesis of the helical coordination chains [M_2(phen)$_2$(chdc)$_2$(H_2O)$_2$] (M = Co(II) and Ni(II)) [49]. In the isomorphous complexes, the metal ion is coordinated to two nitrogen atoms from one phen ligand, three oxygen atoms from two *e,a-cis*-chdc ligands, and one aqua ligand. As the repeat units propagate along the crystallographic 2_1-screw axis (Fig. 13), the right-handed and left-handed helices are alternately packed through further interlinking via hydrogen bonds between the carboxylate and aqua ligands into a centrosymmetric 2D network (Fig. 14). Complex [{VO_2(bpy)}$_2$(1,4-bdc)] consists of zigzag chains built on dinuclear {VO_2(bpy)}$_2$ units linked through 1,4-bdc ligand [50]. These chains are further interconnected through cross-linked hydrogen bonds into a 2D supramolecular network. The hydrothermal reactions of 5-H_2oip with metal acetate salts and bpy gave two complexes [Mn(5-H_2oip)(bpy)]·H_2O and [Zn(5-H_2oip)(bpy)] [51]. In the crystal structures, the metal ions are bridged by carboxylate ligands to form coordination chains that are linked by hydrogen bonds between the phenol group, water molecule

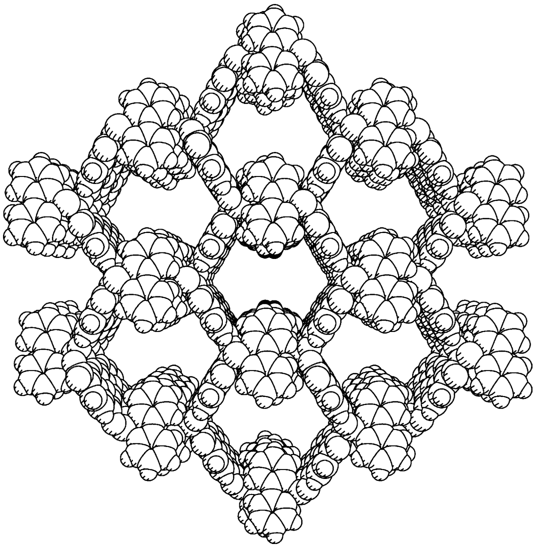


Fig. 15. Space-filling view of the 3D supramolecular network featuring nanosized saddle-like channels in [Zn(bpy)(1,4-bdc)](bpy).

and carboxylate oxygen atoms into layers. Similar architectures were also noted in [Co(Hbtc)(phen)(H_2O)] [32] and [M(Hoa)(bpy)(H_2O)] (M = Co and Mn) [39]. For the alkyl dicarboxylate complex [Cu_2(bpy)$_2$(mal)(H_2O)$_2$](ClO_4)$_2$, the [Cu(bpy)(mal)(H_2O)] and [Cu(bpy)(H_2O)] units are alternately linked by the bis-monodentate mal ligands into a malonate-bridged zigzag chain [52]. The 2D sheet is then formed via hydrogen bonds between the aqua ligands and perchlorate anions. This Cu(II) polymer shows interesting ferromagnetic magnetic behavior.

In [Zn(bpy)(1,4-bdc)](bpy), each 1,4-bdc group acts in a bis-bidentate mode and bridges two zinc ions, resulting in zigzag [Zn(bpy)(1,4-bdc)] chains with the bpy ligands alternately at both sides [53]. These chains are self-assembled into undulating 2D layer via C–H···O hydrogen bonds (3.49 Å) between the phenyl C–H groups and the coordinated carboxy oxygen atoms. Furthermore, all lateral bpy ligands from adjacent undulating [Zn(bpy)(1,4-bdc)] layers are intercalated in an zipper-like fashion via π–π stacking interactions between the bpy groups, in combination with C–H···O hydrogen bonds between the bpy and carboxy groups, to furnish a 3D supramolecular network featuring one-directional nanosized saddle-like channels, as shown in Fig. 15. Curiously, this supramolecular architecture assembled by the weak supramolecular interactions is stable up 190 °C as indicated by thermal gravity measurements [53]. The void contributes to 40.7% of the crystal volume, and is comparable with the most open zeolites, such as the faujasite, paulingite, and zeolite A families [54]. The guest bpy molecules reside in the channels and exhibit parallel, offset intermolecular π−π stacking interactions (face-to-face distance 3.5 Å) between themselves. In [Yb_2(1,2-bdc)$_3$(phen)(H_2O)$_2$]·3.5H_2O, the two independent metal ions are both eight-coordinate; one is bonded to eight oxygen atoms from five 1,2-bdc anions whereas the other is bonded to two nitrogen atoms from one chelate phen and four oxygen atoms from three 1,2-bdc ligands as well as two aqua ligands [27a]. The Yb(III) complex is a 1D coordination polymer connected by 1,2-bdc ligands, the chains are assembled into a 3D network via hydrogen bonds involving the lattice molecules, carboxylate and phen ligands.

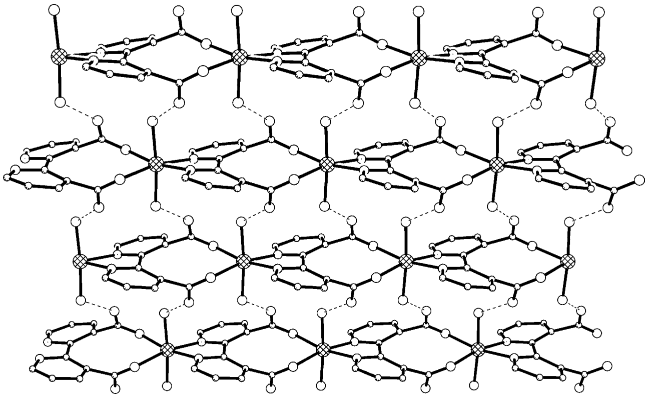


Fig. 16. The 2D supramolecular network of [Co(3,3′-bpyda)(H_2O)$_2$] (adapted from Ref. [55]).

Like 4,4′-bpyda (see Section 2.2), 3,3′-bpyda is also a bridging multidentate ligand having one 2,2′-bipyridine and two carboxylate groups. Two 1D coordination polymers of 3,3′-bpyda, formulated as [Co(3,3′-bpyda)(H_2O)$_2$] and [Ni(3,3′-bpyda)(H_2O)$_3$]·H_2O, were obtained from the reactions of Co(II)/Ni(II) salts and 1,10-phenanthroline-5,6-dione under hydrothermal conditions [55]. The above Co(II) complex has also been synthesized directly from 3,3′-bpyda [56]. In the Co(II) complex, the Co(II) site shows a distorted octahedral geometry; it is coordinated by two nitrogen atoms from one 3,3′-bpyda in a chelating mode and two oxygen atoms from two carboxylate groups, and two aqua ligands; each 3,3′-bpyda ligand uses a pair of nitrogen atoms and two oxygen atoms from two carboxylate groups to bridge two Co(II) atoms so as to generate a linear chain. Hydrogen-bonding interactions between the aqua atoms and uncoordinated carboxylate oxygen atoms extend the chains into 2D supramolecular networks (Fig. 16). In contrast, although the Ni(II) site in the Ni(II) complex also exhibits a distorted octahedral geometry, being ligated by two nitrogen atoms from one 3,3′-bpyda in a chelate mode, one carboxylate oxygen atom and three *cis*-related aqua ligands, only one carboxylate group utilizes one oxygen atom to ligate a Ni(II) ion. In the chains, the repeat units propagate helically by 2_1-screw axis. Such helical chains are extended by hydrogen bonds involving the uncoordinated carboxylate groups, aqua ligands and lattice water molecules into a 2D supramolecular network (Fig. 17).

3.3. *3D architectures based on 2D coordination networks*

Among the few examples of 2D coordination networks organized by hydrogen bonding interactions in the metal

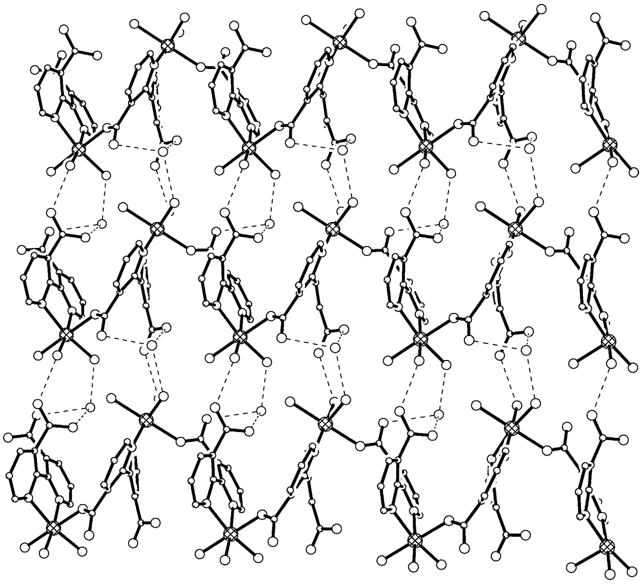


Fig. 17. The 2D supramolecular network of [Ni(3,3′-bpyda)$(H_2O)_3$]·H_2O (adapted from Ref. [55]).

complexes of mixed bpy-like and carboxylate ligands are found several interesting examples. As been mentioned in the earlier sections, dicarboxylates are multidentate ligands (Scheme 2) so that they can easily coordinate to metal ions to furnish 2D coordination polymers. In the presence of interlayer hydrogen bonds, these 2D layers can be further assembled into 3D networks, as illustrated by $[Eu_2(1,4\text{-bdc})_3(\text{phen})_2(H_2O)_2]$, in which a pair of eight-coordinated Eu(III) ions (Eu···Eu distance 4.333 Å) are bridged by four carboxylate ends of the 1,4-bdc ligands into a dimeric unit [27a]; the units are also bridged by 1,4-bdc groups to four adjacent dimeric units to result in an infinite 2D (4,4) network (Fig. 18). The layers are assembled into a 3D supramolecular network via hydrogen bonds between the non-coordinated carboxylate groups and aqua ligands. The analogous $[Yb_2(1,4\text{-bdc})_3(\text{phen})_2(H_2O)]$ [27a], $[Pr_2(1,3\text{-bdc})_3(\text{phen})_2(H_2O)]\cdot 0.5H_2O$ [27b] and $[Nd_2(1,2\text{-bdc})_3(\text{phen})(H_2O)]\cdot H_2O$ [57] complexes were also reported.

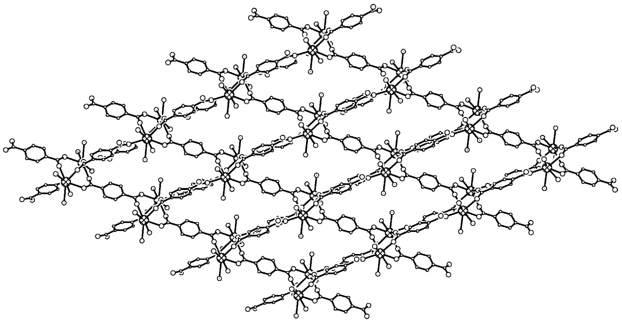


Fig. 18. The (4,4) 2D network in $[Eu_2(1,4\text{-bdc})_3(\text{phen})_2(H_2O)_2]$. The carbon atoms of the phen ligands are omitted for clarity (adapted from Ref. [27a]).

4. Molecular architectures assembled via π–π interactions

Another important supramolecular force in molecular architecture and recognition is π–π interaction engendered by aromatic–aromatic stacking, which enhances the stability of the complexes both in solution state and in solid state. In particular, the π–π stacking interactions in solid state are widely observed in the construction of multi-dimensional structures in offset face-to-face and edge-to-face fashions [58]; combination with coordination bonds, such stacking π–π interactions can be employed to build up interesting coordination supramolecular architectures [11]. In the context of the metal complexes of mixed bpy-like and carboxylate ligands, bpy-like ligands such as bpy, Hobpy, phen and Hophen, play an important role in assembly of high-dimensional networks via stacking π–π interactions.

4.1. 1D, 2D, and 3D architectures based on 0D coordination compounds

From an aesthetic point of view, the assembly of 0D metal complexes such as molecular squares, rhombi or boxes via molecular recognition into multi-dimensional motifs presents an artistic diversion in coordination chemistry. As an important type of supramolecular force, aromatic stacking can be used to control the process of molecular recognition and self-assembly. Based on these concepts, researchers have selected linear, bridging dicarboxylate ligand and planar aromatic chelate ligands to ligate metal ions into coordination aggregates that have cavities large enough to accommodate guest molecules through molecular recognition. The reaction of phen, Na_2su and Mn(II) salt in aqueous methanol yielded centrosymmetric dinuclear complex $[Mn_2(H_2O)_4(\text{phen})_2(\text{su})_2]$ [59] in which the Mn ions are octahedrally coordinated by two nitrogen atoms of one phen ligand, four oxygen atoms from two water molecules and two bis-monodentate su ligands. The dinuclear units are assembled via π−π stacking interactions into supramolecular layers. Other 2D complexes such as $[Mn_2(\text{phen})_2(H_2O)_2(\text{aa})_2]$ [60], $[Cu_2(\text{phen})_2(H_2O)_2(\text{glu})_2]$ [61] and $[\{Fe(\text{sal})_2(\text{bpy})\}_4Ce_2(H_2O)_{11}][\text{Hsal}]_2\cdot EtOH\cdot 3H_2O$ [62] are similarly assembled via π−π interactions.

Coordination networks made from long, bridging ligands can give rise to the formation of large voids as well as to interpenetrating motifs [63], as exemplified by the neutral molecule $[Cu_2(\text{bpa})_2(\text{phen})_2(H_2O)]_2\cdot 2H_2O$ possessing a centrosymmetric tetranuclear rhombic core (Fig. 19) [64], in which each $[Cu(\text{phen})]^{2+}$ unit at a corner is bridged by two bpa ligands in the monodentate–bidentate fashion; the large open rhombic cavity has a 15.1 Å edge and the two diagonals are 16.8 and 25.1 Å. The two pair of phen ligands are extended outward in the four directions of the rhombus, whose two types of corners (acute and obtuse angles) have different functions in the self-assembly into high-dimensional motifs via aromatic π–π interactions. The two lateral phen ligands (each termed as a rod) at the acute angle sites penetrate op-

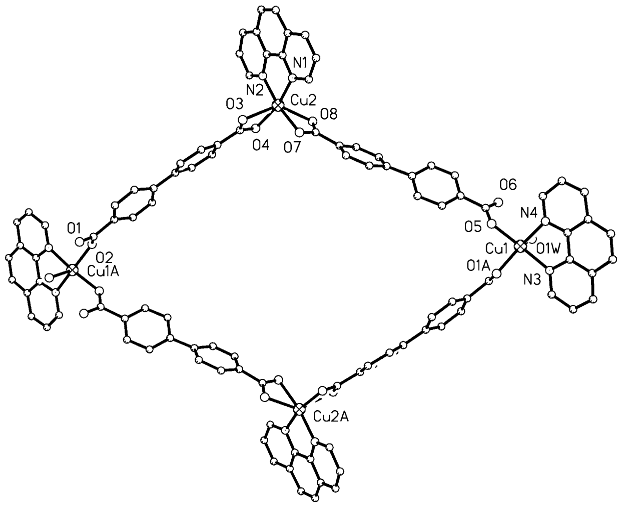
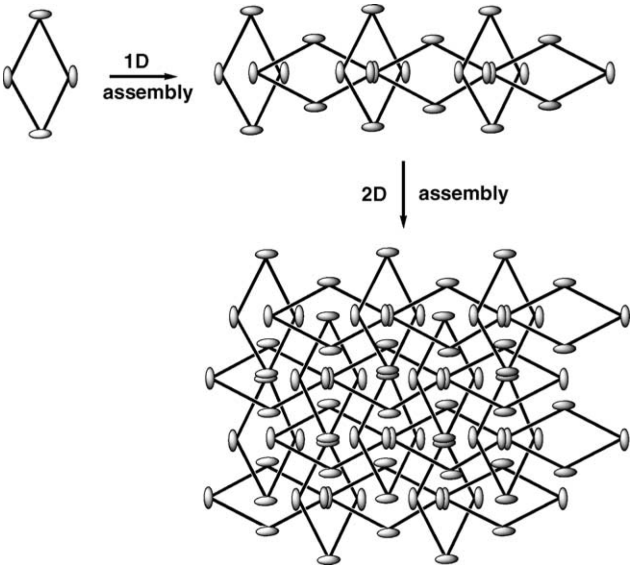


Fig. 19. The molecular structure of $[Cu_2(bpa)_2(phen)_2(H_2O)]_2$ (adapted from Ref. [64]).



Scheme 5. A schematic presentation of the supramolecular assembly of $[Cu_2(bpa)_2(phen)_2(H_2O)]_2$. The ellipsoids and solid lines representing the phen ligands and bpa ligands, respectively.

positely into the rhombic cavity of the third rhombus (termed as a wheel) to generate a molecular node; the aromatic π–π stacking interaction the two rods is strong as the face-to-face distance is 3.46 Å (Fig. 20). Adjacent pairs of rhombi are self-assembled in this way into linear chains. Each pair of phen rods at the acute angle sites of the wheels of the adjacent, parallel chains meet at the rhombic cavities of the perpendicular chains to produce the same molecular nodes, resulting in 2D networks. Each phen group at the acute angle site acts as a rod, and each rhombic cavity functions as a wheel; in fact, the wheel can also be regarded as a stopper. Therefore, each node can be regarded as a pseudorotaxane, an unprecedented structural motif [63]. On the other hand, if the paired phen rods that are strongly stacked within the wheel are regarded as a single rod, the 2D network can otherwise be described as a 2D polyrotaxane formed by interlocking of these rods and wheels. The topology of the 2D polyrotaxane parallels that found in a polyrotaxane constructed by 1D coordination polymers; here, the rods are covalent fragments [65]. Supramolecular interactions such as edge-to-face $C–H\cdots\pi$ interactions between phen protons and bpa phenyl rings ($C–H\cdots\pi$ 3.83 or 4.00 Å), and a hydrogen bond between a phen proton and a carboxy oxygen atom ($C\cdots O$ 3.284 Å) are observed, which may serve as part of the driving forces in the formation of the 2D layers in addition to the π–π stacking interactions. Finally, these 2D layers further stack into a 3D network via aromatic π−π interactions, in which the phen groups at the obtuse angle sites of the rhombi are regularly stacked with each other in an offset fashion with the face–face and centriod–centriod distances at ca. 3.59 and 3.91 Å, respectively (see Scheme 5).

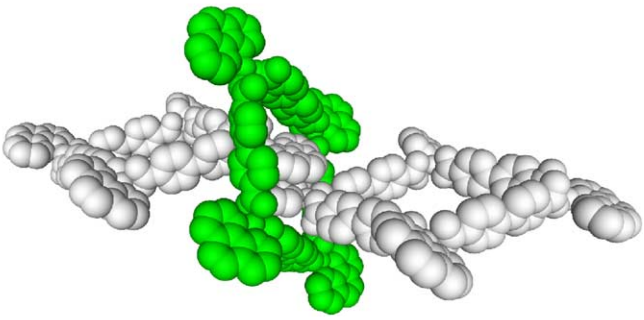


Fig. 20. A space-filling diagram showing the molecular node formed by interpenetration in $[Cu_2(bpa)_2(phen)_2(H_2O)]_2$.

Although both bpy and phen are chemically very stable, under extreme condition, these ligands can undergo unexpected reactions. Recently, hydrothermal reactions of bpy and phen ligands in the presence of Cu(II) ions under basic conditions produced their hydroxylated derivatives. The reaction of Cu(II) salt and phen in the presence of 1,4-H_2bdc in basic solution under hydrothermal condition offered a dumbbell-like $[Cu_4(ophen)_4(1,4\text{-bdc})]$ [66], as shown in Fig. 21. In $[Cu_4(ophen)_4(1,4\text{-bdc})]$, two mixed-valent Cu(I,II) dimers from neighboring molecules are arranged into a parallelogram. In addition, the adjacent aromatic rings of ophen are stacked in an offset fashion with the face-to-face separation of 3.4–3.8 Å. This π−π stacking interaction, together with the intermolecular $Cu^I\cdots Cu^I$ interaction (metal–metal distance 3.37 Å), extend the molecules into a chain motif that is further extended by $C–H\cdots O$ hydrogen bonds between the aromatic groups and carboxylate groups from adjacent chains ($C\cdots O$ 3.41 ∼ 3.48 Å) into a 3D supramolecular array. Replacing the 1,4-bdc ligand by bpa led to the corresponding tetranuclear complex $[Cu_4(ophen)_4(bpa)]$ [67], while replacing phen by bpy gave $[Cu_4(obpy)_4(1,4\text{-bdc})]$ [66,67]. The hydroxylation is a new reaction under hydrothermal conditions, and can be employed to prepare the new bpy-like ligands that are good candidates for photoluminescent [68]

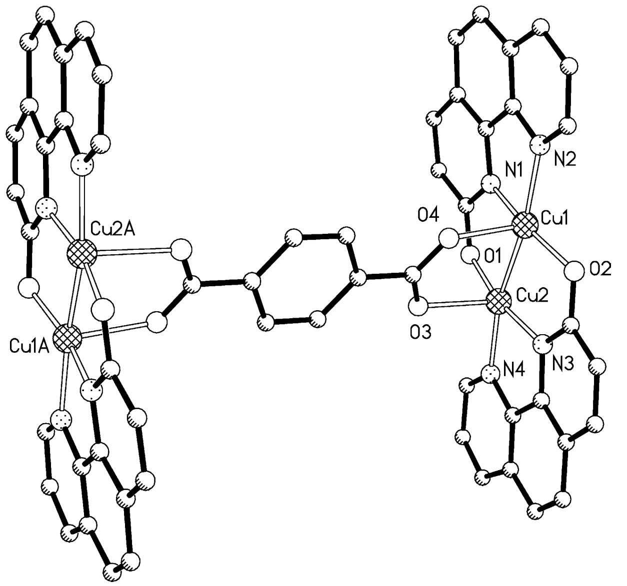


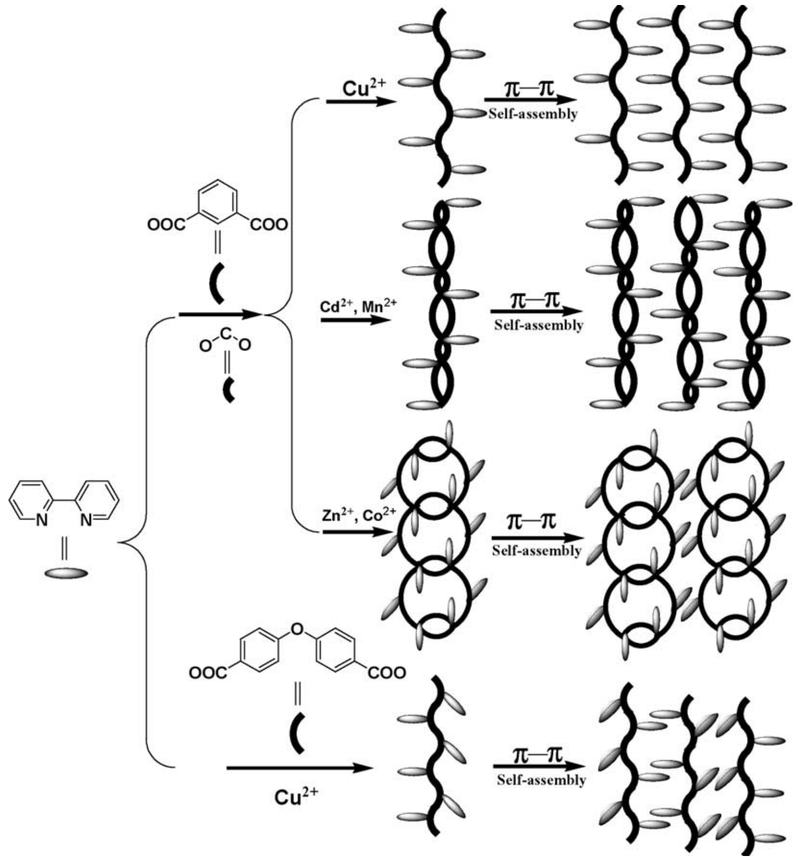
Fig. 21. Molecular structure of [Cu_4(ophen)$_4$(tp)] (adapted from Ref. [66]).

and conducting materials [69]. Another centrosymmetric dinuclear compound displaying a 3D network constructed by $\pi-\pi$ interactions, [Cu_2(phen)$_4$(mal)$_2$] has also been reported [70].

4.2. Double-strand helices, zippers, 2D and 3D architectures based on 1D coordination polymers

As flexible or V-shaped bridging organic bridges improve the helicity of polymeric chains, a suitable choice of flexible or V-shaped dicarboxylate bridges can be particularly effective in the formation of single-strand helical chains in the presence of aromatic chelate ligands, such as bpy and phen. These heterocyclic chelates are critical to maintaining one dimensionality; furthermore, they can provide supramolecular recognition sites for $\pi-\pi$ aromatic stacking interactions that can lead to multi-strand helices or zippers.

By using bpy and the V-shaped 1,3-bdc ligand, the reaction of metal salts under hydrothermal conditions afforded the infinite, linear coordination polymers [Cu(1,3-bdc)(bpy)]·$2H_2O$, [M_2(1,3-bdc)$_2$(bpy)$_2$] (M = Zn, Co, Cd or Mn) and [Cu_3(1,3-bdc)$_2$(1,3-Hbdc)$_2$(bpy)$_2$] [71–74], for which three different structural motifs have been summarized in Scheme 7. In [Cu(1,3-bdc)(bpy)]·$2H_2O$, each Cu(II) ion is coordinated by two oxygen atoms from two bis-monodentate 1,3-bdc ligands and two nitrogen atoms from a chelate bpy to furnish a distorted square-planar geometry. Adjacent Cu(II) ions are bridged by a 1,3-bdc ligand to form a handed helical chain running along a crystallographic 2_1-axis with a long pitch of 11.25 Å, as shown in Fig. 22. These chains are decorated with bpy ligands alternately at two sides in



Scheme 6. Some structural motifs of 1D polymers assembled by V-shaped dicarboxylate bridges in the presence of bpy-like ligands.

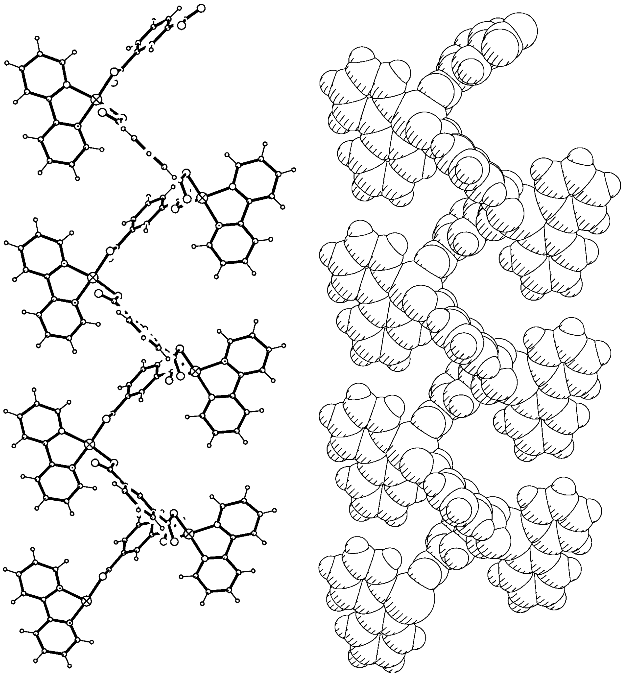


Fig. 22. The single-strand helical chain in [Cu(1,3-bdc)(bpy)]·$2H_2O$ (adapted from Ref. [71]).

an outward fashion and are further extended into a 2D networks via intercalation between the lateral bpy ligands from adjacent layers in a zipper-like fashion. The zipper-like style (Scheme 6), in which the bpy ligands are arranged in an offset fashion with a face-to-face distance of ca. 3.43 Å, indicates significant π−π stacking interactions. The phenyl rings of the 1,3-bdc of the helix are arranged in a parallel fashion, being separated from each other by 8.29 Å. Adjacent helices are racemically packed through intercalation of the lateral 1,3-bdc phenyl rings in an off-set, zipper-like fashion with the short and longer face-to-face distances of 3.32 and 4.97 Å into layers [71]. Lowering the pH of the reaction gave another 1D polymer [$Cu_3(bpy)_2(1,3\text{-bdc})_2(1,3\text{-Hbdc})_2$], which consists of trinuclear units [73]. These chains are further extended into 2D layers via aromatic π−π stacking interactions as well as hydrogen-bonding interactions between the free carboxylic and carboxylate groups.

When the Cu(II) ion was replaced by Zn(II) or Co(II) ions, structurally different complexes were also obtained. For example, in [$Zn_2(1,3\text{-bdc})_2(bpy)_2$] there are two different metal coordination environments [72]. One Zn(II) ion is coordinated by two oxygen atoms from one chelating carboxylate end of one 1,3-bdc ligand, two oxygen atoms from two μ-carboxylate ends of two 1,3-bdc ligands and two nitrogen atoms from a chelate bpy ligand to furnish a grossly distorted octahedral environment. The other Zn(II) ion is ligated by four oxygen atoms from two chelating carboxylate ends of two 1,3-bdc ligands and two nitrogen atoms from a chelate bpy ligand to complete a highly distorted octahedral geometry. The first Zn(II) ion is bridged by two μ-carboxylate ends to a crystallographically equivalent metal ion to generate a dinuclear unit. The dinuclear units are connected to four mononuclear sites through four 1,3-bdc ligands to furnish coordination ribbons, which exhibit large rings each comprising four bridging 1,3-bdc ligands, two dinuclear units and two mononuclear units as shown in Fig. 23. The ribbon is decorated by bpy ligands that point outward in four different orientations and, most probably, contributed to the manner of adjacent ribbon chains packing into a 3D network through π−π stacking interactions (face-to-face distance is ca. 3.56 or 3.62 Å) [72,74]. In contrast, for [$M_2(1,3\text{-bdc})_2(bpy)_2$] (M = Cd, Mn) [72,74], the bpy ligands are decorated at both sides of the helical ribbons (Fig. 24). Adjacent ribbons are intercalated in a zipper fashion into 2D layers through the π−π stacking interactions between the bpy ligands with the face-to-face distances of ca. 3.47–3.64 Å, as shown in Scheme 6. From these studies, we can deduce that the Cu(II) ion prefers a four- or five-coordinate, whereas Zn(II), Co(II), Cd(II) and Mn(II) prefers a six-coordinate environment, i.e., chain structures based on a mononuclear or trinuclear (Cu), tetranuclear (Zn and Co), or binuclear (Cd and Mn) units. Consequently, the coordination behavior of the metal ions has a pronounced affect on the formation of building units as well as on self-assembly into higher dimensional networks.

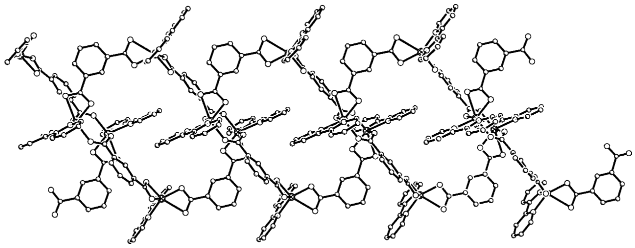


Fig. 23. The one-dimensional ribbon in [$Zn_2(1,3\text{-bdc})_2(bpy)_2$] (adapted from Ref. [72]).

Flexible V-shaped oba yields [Cu(oba)(bpy)] [71] in which the Cu(II) ion is coordinated by four oxygen atoms from two bis-bidentate oba ligands and two nitrogen atoms from a chelating bpy to furnish a distorted octahedron around the metal ion. Each pair of adjacent Cu(II) ions is interconnected into a helical chain by the oba bridges. The bpy ligands are extended outward from the sides of the chain, but the planes of every two adjacent bpy ligands are perpendicular to each other (dihedral angle ca. 89.3°). The lateral bpy ligands from adjacent chains are paired to furnish only moderate strong

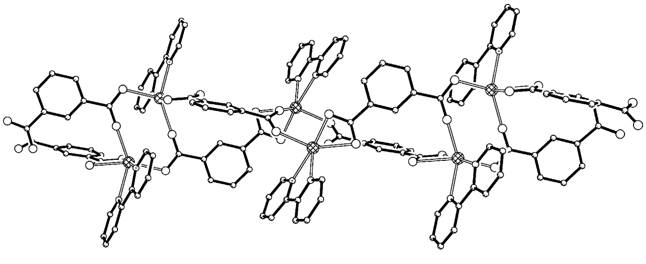
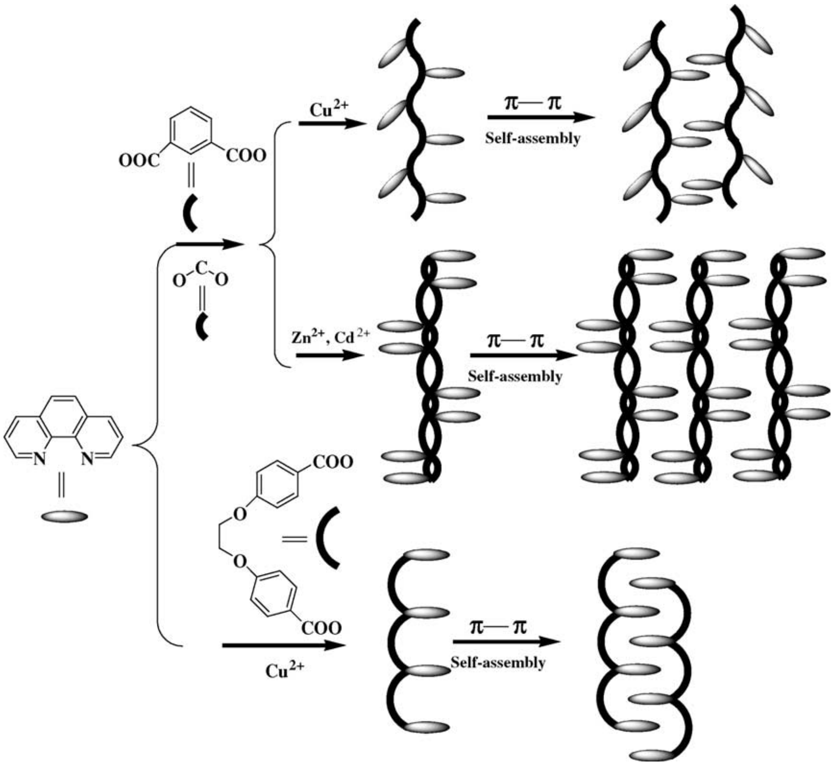


Fig. 24. The one-dimensional ribbon in [$Cd_2(1,3\text{-bdc})_2(bpy)_2$] (adapted from Ref. [72]).



Scheme 7. Some structural motifs of 1D polymers assembled by flexible or V-shaped dicarboxylate bridges in the presence of phen ligands.

π−π stacking interactions in an offset fashion with a face-to-face distance of ca. 3.58 Å, which extends the helical chains into undulating layers (Fig. 25).

The use of the somewhat bulkier phen in place of bpy led to other interesting supramolecular architectures (summarized in Scheme 7). Treatment of a Cu(II) salt with 1,3-bdc in the presence of phen offered $[Cu_2(1,3\text{-bdc})_2(phen)_2(H_2O)]$ under hydrothermal conditions, whose structure is similar to that of the neutral single-strand helix found in $[Cu(1,3\text{-bdc})(bpy)]\cdot 2H_2O$ [71]. Two different coordination environments for Cu(II) are noted in $[Cu_2(1,3\text{-bdc})_2(phen)_2(H_2O)]$. One Cu(II) ion is coordinated by two oxygen atoms from two bis-monodentate 1,3-bdc ligands and two nitrogen atoms from a chelate phen to furnish a distorted square-planar coordination; the remaining carboxyl oxygen atoms interact weakly with the Cu(II) ion at the axial sites. The other Cu(II) ion is ligated by two oxygen atoms from two bis-monodentate 1,3-bdc ligands and two nitrogen atoms from a chelating phen at the basal positions, and the square-pyramidal N_2O_2O' geometry is completed by an aqua oxygen atom at the apical position. The 1,3-bdc ligands bridge a pair of adjacent Cu(II) ions into a helical chain that has a 16.38 Å pitch. The phen ligands are alternately attached on either sides of a single-strand helical chain, and are oriented either approximately parallel or perpendicular to the general axis of the chain. The roughly perpendicular orientation of a half of the phen ligands allows for the pairing of two inversely related single-strand helical chains into a double-strand zipper-like ribbon under the influence of aromatic π–π interactions at a face-to-face distance of 3.37 Å between the phen pairs (Fig. 26). The double-strand zippers are further extended through aromatic π–π interactions, hydrogen bonds between the aqua ligands (and aromatic groups as well) and carboxylate oxy-

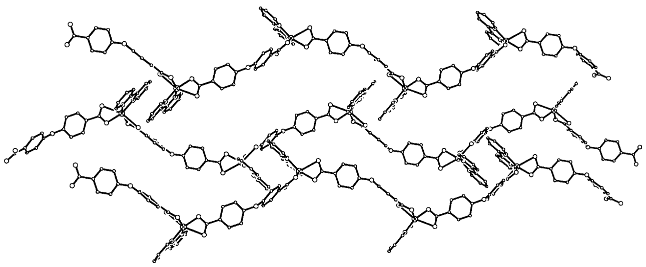


Fig. 25. The 2D network in [Cu(oba)(bpy)] (adapted from Ref. [72]).

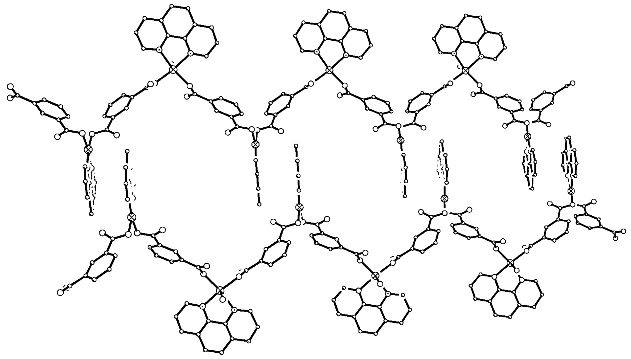


Fig. 26. A pair of the helical chains in $[Cu_2(1,3\text{-bdc})_2(phen)_2(H_2O)]$.

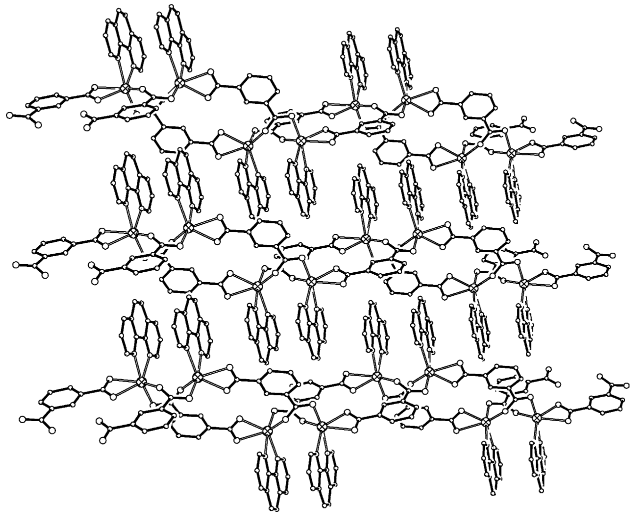


Fig. 27. The 2D networks formed by π–π stacking interactions between the phen groups from adjacent chains in [Cd(1,3-bdc)(phen)] (adapted from Ref. [72]).

gen atoms, and also by van der Waals interactions, into the final 3D architecture.

Lowering the pH value led to the isolation of polymeric $[Cu_3(phen)_2(1,3\text{-bdc})_2(1,3\text{-Hbdc})_2]$, a trinuclear compound [73]. The polymeric chains are further extended into 2D layers via aromatic π−π interactions as well as by hydrogen bonds between a pair of uncoordinated carboxy groups; isomorphous [M(1,3-bdc)(phen)] (M = Cd or Zn) were similarly synthesized [72]. In [Cd(1,3-bdc)(phen)], the two Cd(II) ions that related by a two-fold axis are bridged by a pair of the 1,3-bdc μ-carboxylate ends into a dinuclear unit; the intradimer Cd· · ·Cd distance is 3.99 Å and the unit has two phen ligands at one side at a face-to-face distance of 3.51 Å. The V-shaped 1,3-bdc ligand further acts in the chelate-bidentate coordination mode to link the adjacent Cd(II) ions into 1D ribbons based on a double-strand helix that has a 9.55 Å pitch (Fig. 27). The adjacent zigzag ribbons are packed through intercalation of the lateral phen ligands at a face-to-face distance of 3.32 Å in a zipper-like fashion into 2D networks. Adjacent ribbons interact strongly through π−π interactions between the 1,3-bdc phenyl rings in an offset fashion at a face-to-face distance of ca. 3.38 Å, the interactions further extending the 2D network into a 3D architecture. In [Zn(1,3-bdc)(phen)], the Zn(II) ion exists in a distorted trigonal-bipyramidal arrangement as it is coordinated by two nitrogen atoms from a chelating phen ligand and three oxygen atoms from two μ-carboxylate ends and one monodentate carboxylate end of a 1,3-bdc ligand; the 1,3-bdc ligand exhibits monodentate–bidentate coordination behavior. Although the coordination environments of metal ions are different between [Cd(1,3-bdc)(phen)] and [Zn(1,3-bdc)(phen)], the packing modes of the complexes are similar.

The oba ligand, which has longer arms, afforded, under similar reaction conditions, complexes [Cu(oba)(phen)] [71] and $[Co(oba)(phen)(H_2O)]$ [44] that display a double-strand helical conformation. In [Cu(oba)(phen)], the Cu(II) ion is only four-coordinate through bonding to two oxygen atoms from two oba ligands and a bidentate phen; the oba ligands connect the Cu(II) ions into a helix that has a 12.06 Å pitch (Fig. 28). The phen ligands are extended in a parallel fashion on both sides of the single-strand chain at a face-to-face distance of 6.84 Å to give a spatial arrangement that is suitable for aromatic intercalation. In fact, each pair of independent and two-fold-axis-related, homochiral polymeric chains intertwine with each other into an unusual double-strand helix of C_2 symmetry though the π–π stacking interactions between the phen ligands. The face-to-face separation between the inter-strand phen ligands in the double helix is 3.42 Å. Both left- and right-handed helices coexist in the racemic complex. Aside from an example of two single-strand helicates intertwined to form infinite double helices [75], [Cu(oba)(phen)] represents an example of a neutral double-helix assembled by single-strand helical coordination oligomers whose assembly has been directed by π−π aromatic stacking.

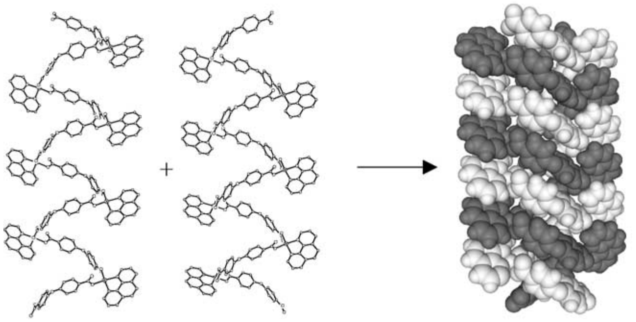


Fig. 28. A double-strand helix generated by intertwining of two single-strand helical chains in [Cu(oba)(phen)] (adapted from Ref. [71]).

When Co(II) was used in place of Cu(II), the resulting complex, $[Co(oba)(phen)(H_2O)]$ [44], displays two single-strand helical chains which interact through hydrogen bonds to generate a double-strand chain (shown previously in Fig. 12b). The arrangement differs from that of [Cu(oba)(phen)] in that two single-strand helices intertwine into a double-strand ribbon [71], the difference arising from the different coordination environments of Co(II) and Cu(II) ions as well as compositions. The high-coordination number Cd(II) complex, $[Cd_3(phen)_3(oba)_2(Hoba)_2(H_2O)_2]$ [44], consists of a centrosymmetric trinuclear subunit with one Cd(II) ion located at the center. This Cd(II) ion is eight-coordinate in a environment composed of four oxygen atoms from two bidentate ends of the bidentate–tridentate oba ligands, two nitrogen atoms from a chelating phen molecule and two oxygen atoms from two water molecules. The other Cd(II) ion is seven-coordinate through bonding with five oxygen atoms from the oba carboxylate groups and two nitrogen atoms from a chelating phen ligand; two of them are bridged by two carboxylate groups as well as by π−π stacking interactions (face-to-face 3.55 Å) of phen ligands. A pair of the bidentate-chelating and bidentate-bridging oba ligands con-

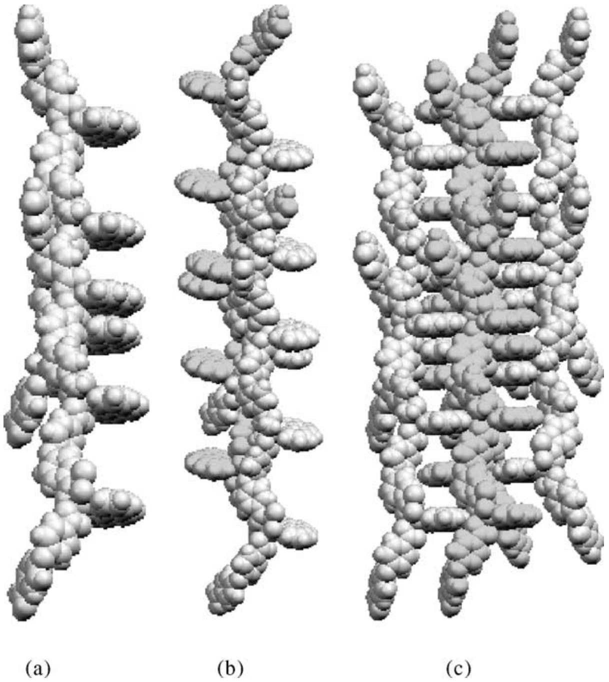


Fig. 29. Perspective views of the single chain (a), double-strand chains (b), and 2D network (c) in $[Cd_3(phen)_3(oba)_2(Hoba)_2(H_2O)_2]$ (adapted from Ref. [44]).

nect the ions into a polymeric chain in which the phen ligands are attached to one side of the chain (Fig. 29a). Two adjacent single-strand chains wrap together via strong π−π stacking interactions (face-to-face 3.55 Å) between the aromatic groups of the oba ligands and hydrogen bonds to generate double-strand ribbons; the phen ligands are attached to both sides of the ribbons (Fig. 29b). Adjacent double chains are packed through intercalation of the lateral phen ligands in a zipper-like fashion into a layer (Fig. 29c). The protonated carboxylic ends are almost perpendicular to the layer; they are linked together and they extend the layers into a 3D network via hydrogen bonding interactions.

The more flexible dicarboxylate ligand, eoba, offers further insight on the influence of the dicarboxylate moiety on the resulting supramolecular arrangement [71], as indicated by [Cu(eoba)(phen)], which has a flexible chain structure. The eoba ligands connect the Cu(II) ions to furnish such a chain in which adjacent ions are separated by 14.936 Å. The phen ligands are decorated at one side of this chain in a slanted fashion but as these recognize those from another chain through offset aromatic π−π stacking interactions at a face-to-face separation at ca. 3.34 Å, a zipper-like, double-strand chain (Fig. 30) is formed.

Based on the above observations, we can conclude that the most critical factors for the pairing of single-strand helical coordination chains into double-strand helices brought about by π–π interactions lies in the coordination behavior of the metal ion, the length and flexibility of the dicarboxylate ligand as well as the suitability of bpy-like ligands for π−π stacking interactions. In the above investigations, the coordination modes of the metal ions are different, which implies that a Cu(II) ion with a distorted square-planar geometry is essential for the formation of double-strand helices assembled largely by π–π interactions between the aromatic chelating ligands. The long-armed, V-shaped dicarboxylate ligand, oba, in [Cu(oba)(phen)] is twisted in such a way that the two phenyl rings are roughly perpendicular (dihedral angle = 74°); phen ligand is slanted with respect to the axis of the helix (ca. 60°). At such an optimized helical conformation, two single-strand helical chains can recognize each other and can therefore twine together under the direction of the supramolecular interactions to form the double-strand chain in [Cu(oba)(phen)]. In contrast, the 1,3-bdc ligand is much more rigid, so that the bpy units in $[Cu(1,3\text{-bdc})(bpy)]\cdot 2H_2O$ are oriented along this axis, an orientation that is not favorable for a double-strand helix to be formed. The presence of the larger aromatic phen ligands further enhances π−π aromatic stacking interactions, as noted in the double-strand helices of $[Cu_2(1,3\text{-bdc})_2(phen)_2(H_2O)]$. This observation underscores the importance of supramolecular interactions in the formation of the double-strand helices.

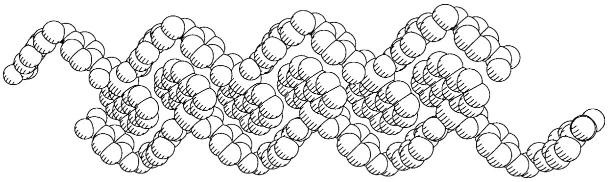
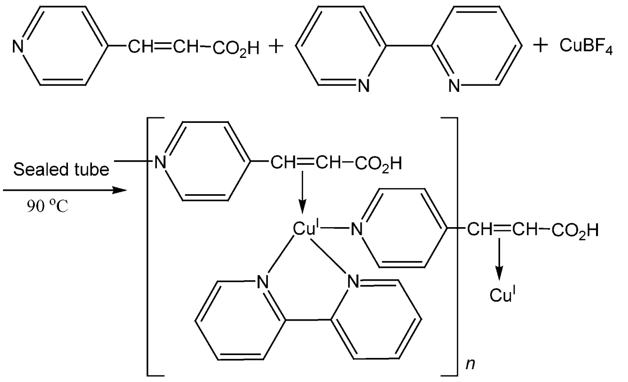


Fig. 30. The zipper-like double-strand chain in [Cu(eoba)(phen)] (adapted from Ref. [71]).

Relevant polymeric coordination chains, such as $[Cu_2(btac)(phen)_2]\cdot H_2O$, $[Cd_4(btac)_2(phen)_4(H_2O)_4]$ [76], $[Cd_2(Hbtc)_2(phen)_2]_2[Cd(Hbtc)(phen)_2]$ and $[Cd(1,4\text{-bdc})(phen)(H_2O)]$ [77], and $[Cu(phen)(btac)_{0.5}]\cdot H_2O$ [78], connected by aromatic polycarboxylate and further assembled into 3D network via π−π stacking interactions were also observed.

The carboxylate ligands, 3-hpya and 4-hpya, possess an ethylene group, a feature that leads to the assembly of the 1D coordination polymers via the coordination of the olefinic group [79,80]. Solvothermal treatment of 4-hpya, bpy and $Cu(MeCN)_4(BF_4)$ gave $[Cu(bpy)(4\text{-hpya})](BF_4)$ (see Scheme 8); the Cu(I) ion is four-coordinate in a distorted tetrahedral environment of three nitrogen atoms (two from bpy and one from 4-hpya) and the C–C portion of 4-hpya. The 4-hpya ligand links two Cu(I) ions by an N atom and an olefin unit to give rise to a 1D coordination polymer. More importantly, the chains are assembled into a 3D coordination network via π−π interactions. This complex displays strong red luminescence with a maximum at ca. 647 nm at room temperature.

Complex [Mn(tda)(bpy)] is a 1D ribbon formed by binuclear Mn_2 units in the appearance of the classic paddle-wheel ‘copper acetate’ core [81]. A chelating bpy completes the approximately trigonal-prismatic environment around the Mn(II) ion. Adjacent ribbons intercalate into a 3D net-



Scheme 8. The synthesis and structure of [Cu(bpy)(4-hpya)](BF_4).

work via π−π stacking interactions of the bpy ligands. This complex exhibits antiferromagnetic behavior. Other polymeric chains assembled by alkyl dicarboxylates include $[Cu(bpy)(Haa)]_2(aa)\cdot 6H_2O$ [82], $[M_2(H_2O)_2(phen)_2(pa)_2]\cdot 4H_2O$ (M = Mn or Cu) [83], $[Mn(phen)_2(Hsub)]_2(sub)\cdot H_2sub$ [84], [Mn(phen)(mal)] [85a] and [Ln(glu)(phen)Cl] (Ln = Tb or Ho) [85b]. These chains are also further assembled into layers or 3D framework via π−π stacking interactions.

The crystal structure of $[Ag(\mu_3\text{-}3,3'\text{-Hbpyda})(H_2O)]$ [86] consists of linear chains in which the metal ion is coordinated in a distorted tetrahedral environment this is composed of one aqua ligand, two pyridyl groups from two different 3,3′-Hbpyda ligands and one oxygen atoms from the carboxy group of the third Hbpyca ligand. Each monoprotonated 3,3′-Hbpyda ligand functions in the uncommonly found μ_3-mode (*N*, *N*′, *O*) mode to bridge three Ag(I) ions; the two pyridyl rings do not behave in the usual planar, chelating mode.

The nta ligand is a versatile building block having seven potential donor atoms; the three carboxylate groups exist in an approximate T-shape conformation, which is a necessary requirement for a ladder structure. Such coordination geometry has been realized in $[Zn_2(bpy)(nta)Cl]\cdot H_2O$, whose two independent zinc ions are both in distorted trigonal-bipyramidal environments [87]. One Zn(II) ion is coordinated by two nitrogen atoms from one bpy ligand and three oxygen atoms from two different nta ligands whereas the other Zn(II) ion is coordinated by one chloride ligand, one nitrogen and three oxygen atoms from one nta ligand. The T-shaped $[Zn(nta)Cl]^{2-}$ units are connected by the $[Zn(bpy)]^{2+}$ nodes into an infinite ladder framework (Fig. 31). Intercalation between the lateral bpy ligands from adjacent ladders in a zipper-like fashion through the π−π stacking interactions leads to a layer structure.

4.3. 3D architectures based on 2D coordination networks

1,2,4,5-Benzene-tetracarboxylate (btac) is an excellent ligand for the assembly of layer structures. In $[Co_2(bpy)_2(H_2O)(btac)]$ [88], each Co(II) ion coordinates to two nitrogen atoms of one bpy, three oxygen atoms of two different carboxylate groups and one oxygen atom of a water molecule (Fig. 32). The two Co(II) are linked by two carboxylate groups of the btac ligands to form a ladder-like chain. Neighboring chains are connected together by μ-H_2O bridges into a new, chiral 2D (6,4)-network. The chains propagated by two-fold screw axes. The 2D layers are further assembled into a 3D network via π−π stacking interactions of the bpy ligands. Hydrothermally synthesized $[Fe_2(phen)_2(\mu_6\text{-btac})]$ [89] also consists of polymeric layers with the [Fe(phen)] fragments bridged by the btac ligands. The polymeric layers are arranged in an ···ABAB··· fashion via π−π stacking interaction of the phen groups into a 3D framework. Complex $[Co_2(btc)(bpy)_2(H_2O)]$ is a layer coordination polymer constructed by μ-H_2O bridges and further

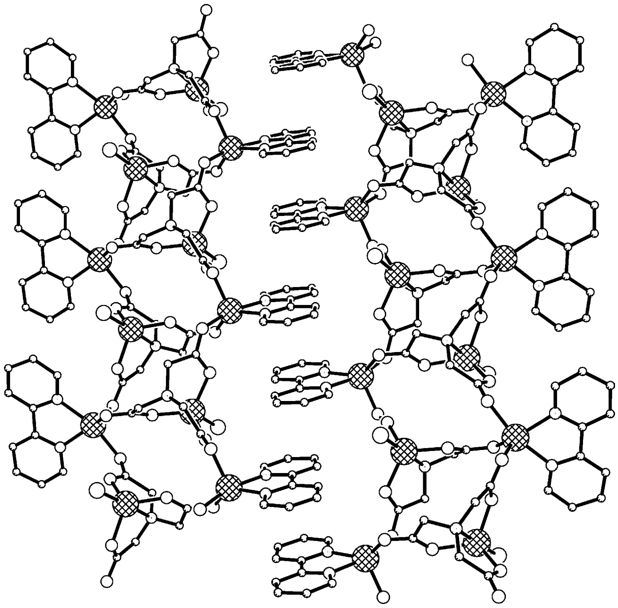


Fig. 31. Structure of $[Zn_2(bpy)(nta)Cl]\cdot H_2O$.

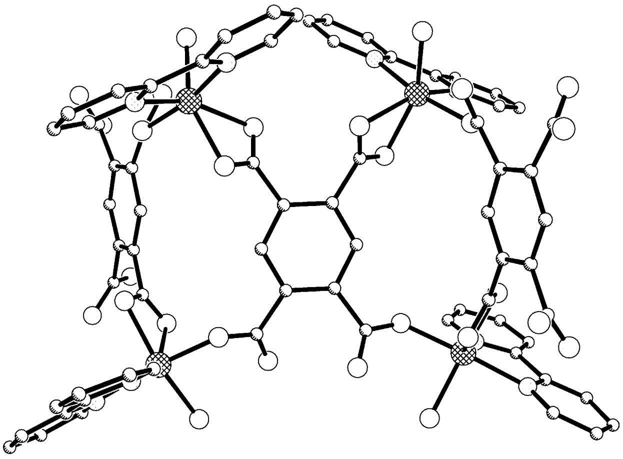


Fig. 32. The coordination environments in $[Co_2(bpy)_2(H_2O)(btac)]$ (adapted from Ref. [88]).

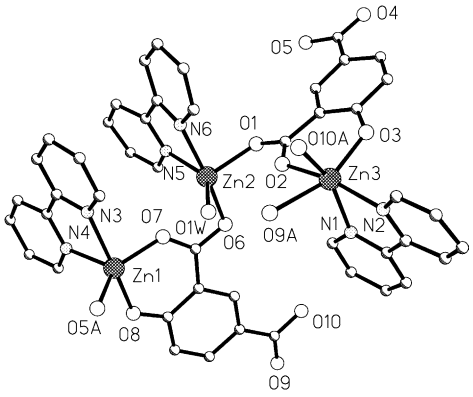


Fig. 33. The coordination environments in $[Zn_3(bpy)_3(4\text{-oip})_2]\cdot 5H_2O$ (adapted from Ref. [91]).

assembled into a 3D network via π–π stacking interactions [90].

The reactions of metal salt with 4-H_3oip and bpy under hydrothermal conditions offered $[Zn_3(bpy)_3(4\text{-oip})_2]\cdot 5H_2O$ and $[Co_3(bpy)_3(4\text{-oip})_2]\cdot 5H_2O$ [91]. The zinc(II) complex crystallizes in the chiral $P2_1$ space group. In the structure of the Zn(II) complex, each asymmetric unit consists of three Zn(II) ions (Fig. 33); two are five-coordinate, whereas the third is six-coordinate, and the metal centers are bridged via two carboxylate groups. Each trinuclear cluster is further connected to four other clusters via four 4-oip bridges to form a two-dimensional network having a (4,4) topology and cavities of ca. 5.5 Å × 6.0 Å (van der Waals radii of the atoms removed) (Fig. 34). Lattice water molecules were filled in the cavities. The bpy is coordinated to the five-coordinate Zn(II) ions points towards the upper layer and the bpy bound to the six-coordinated Zn(II) to the lower layer. On the other hand, the layers are stacked in an $\cdots$ABAB$\cdots$ pattern into a 3D network. The Co(II) complex is isostructural with the Zn(II) complex.

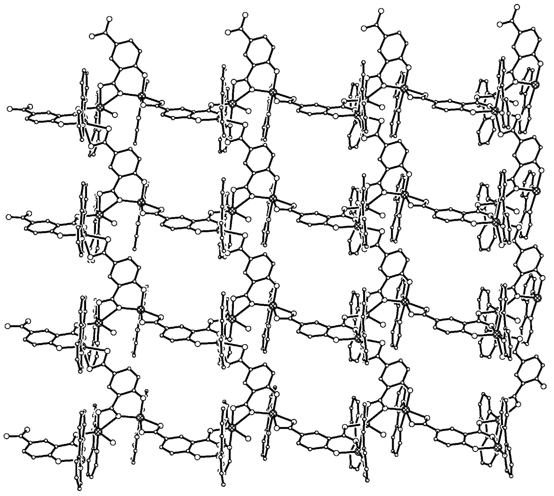
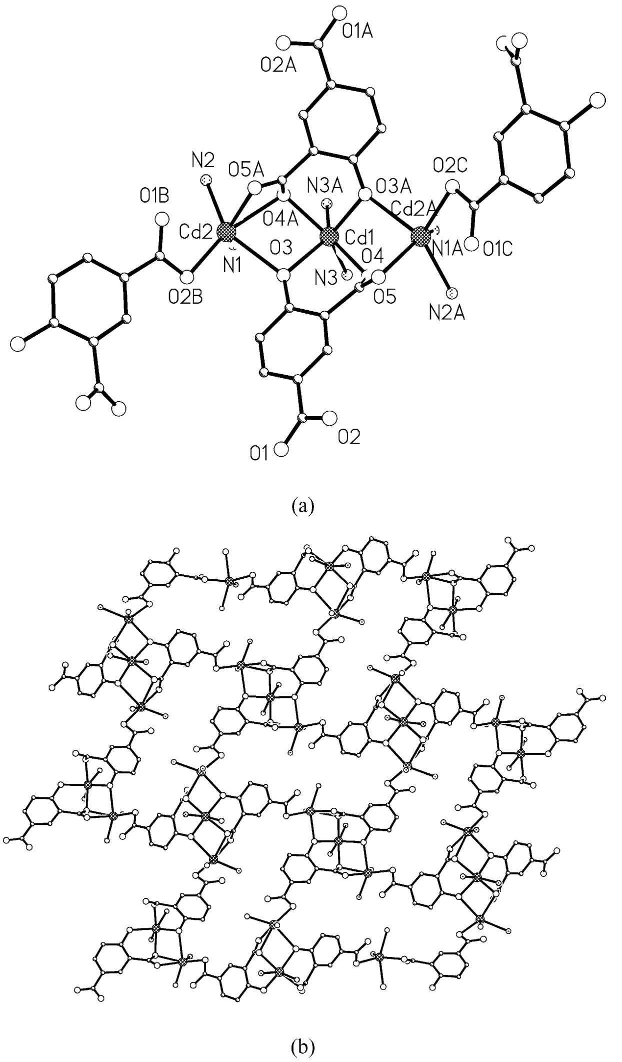


Fig. 34. The 2D layer of $[Zn_3(bpy)_3(4\text{-oip})_2]\cdot 5H_2O$ (adapted from Ref. [91]).



(a)

(b)

Fig. 35. Perspective views of the coordination environment (a) and 2D network (b) of $[Cd_3(bpy)_3(4\text{-oip})_2]$ (adapted from Ref. [91]).

In $[Cd_3(bpy)_3(4\text{-oip})_2]$, one Cd(II) ion is located at a two-fold axis and shows a distorted octahedral geometry (Fig. 35a); it is connected to two adjacent Cd(II) ions via an OH bridge and a monatomic carboxylate bridge into a trinuclear cluster. Each cluster is further connected to four neighboring clusters via four hip ligands to furnish a 2D network with a (4,4) topology (Fig. 35b). The chelating bpy ligands of the trinuclear cluster point to one side of the layer, i.e., the layers pack in an $\cdots$AAA$\cdots$ fashion the 3D network [91]. The use of H_3sip and H_3bta ligands in place of 4-H_3oip afforded the complexes $[Cd_3(sip)_2(bpy)_4(H_2O)_2]\cdot 2H_2O$ and $[Co_3(phen)_2(H_2O)_2(bta)_2]$ [92,93].

Complex $[Co_2(phen)_2(fum)_2]$ consists of dimeric units doubly bridged by carboxylate groups in a *syn–syn* fashion [94]. Each metal is further connected through the fum anions to form corrugated sheets having a (4,4) topology. Such layers are packed into a 3D framework through the intercalation of the phen ligands. In $[Cu_2(phen)_2(sub)_2]\cdot 3H_2O$, dinuclear units are interlinked by the tridentate sub ligands to form layers and these are further assembled via π−π stacking interactions into a microporous 3D network; the H_2O molecules reside in the tunnels [95].

5. Conclusions and outlook

As with those of other organic ligands, the coordination polymers of both carboxylate and bpy-like ligands exhibit a diverse range of interesting structural motifs. The accumulated crystallographic data show that in the presence of chelating bpy-like ligand, the dimensionality of the coordination-bonded polymers is decreased in a number of compounds. On the other hand, the dimensionality of the coordination polymers may be increased by employing higher coordinate metal ions or multinuclear structural units as the building blocks; these manifest themselves as highly connected nodes in the polymeric structures. The presence of both carboxylate and bpy-like ligands may lead to supramolecular interactions of the hydrogen-bonding and π−π stacking types. Rational combinations of the bridging carboxylates, bpy-like chelate ligands, and metal ions should, in principle, allow for generation of interesting coordination molecular architecture targets based on coordination bonding, and supramolecular interactions, as noted by the double-helices, molecular zippers and other architectures.

Although the synthesis of such coordination architectures having certain useful properties requires further exploration, a number of coordination architectures summarized in this review exhibited interesting physical properties including magnetic, non-linear optical, photoluminescent properties.

We may expect that with a rational design, more unusual coordination architectures such as with a mixed-ligand system will be possible that can also possess properties that will find potential applications; the outcome of such designed syntheses will be expected to have tremendous importance to supramolecular chemistry and crystal engineering.

Acknowledgements

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