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Review

Coordination polymer networks with O- and N-donors: What they are, why and how they are made

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Contents

Abstract

With this review on metal ion containing coordination polymer networks, we wish to highlight the current research in the field by giving a short overview on the concept of coordination polymers networks, how and why they are made. Several reviews on different aspects of coordination polymer compounds will be grouped and shortly presented in the introduction. Recent typical examples for different dimensionalities of the networks

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will be presented as well as representative compounds for specific applications. One focus will also be the problematic of polymorphism, respectively, supramolecular isomerism and pseudo-polymorphism or solvates. With a view to the large number of polymer coordination compounds that can be found in the literature, we will limit the review to the more recent results in the field and restrain the examples to the more common O-donor and mainly N-donor ligands. As our own interests lie in the field of group 11 elements, some focuses are more related with this field.

The expression “Coordination Polymer” was first used by J.C. Bailar in 1967, when he compared organic polymers with inorganic compounds which can be considered as polymeric species. In comparison he established rules for the building and the required properties of new species involving metal ions and organic ligands [J.C. Bailar Jr., Prep. Inorg. React. 1 (1964) 1]. During the last 15 years the number of publications concerning coordination polymers has dramatically increased from 100 articles per year to 1000 in 2004. What really are coordination polymers? Why do these huge developments happen?

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Keywords: Coordination polymer networks; N-donor ligands; Applications; Synthesis; Solid state structures

1. Introduction: about coordination polymers

Polymers are defined as high molecular weight molecules formed by the repetition of monomeric units linked with covalent bonds. In comparison, coordination polymers [1] are infinite systems build up with metal ions and organic ligands as main elementary units linked via coordination bonds and other weak chemical bonds. These compounds are also named metal-organic coordination networks or metal-organic frameworks (MOF) in the case of ordered structures [2].

For the chemist, polymeric coordination networks syntheses could be considered as “construction games”: the final architecture depends on the building modules (organic ligands, metal centres, their counter ions and solvent molecules) and their compatibilities. Analyses of the final geometries, of the diverse interactions and optimization of the growth processes are described as crystal engineering. In appropriate circumstances, crystals can be considered as the sum of a series of reproducible molecular recognition events. This means that control of the overall arrangement of the modules can be conceivable with prediction of topology and dimensionality, but not of the exact crystal structure (cell parameters). This approach can be compared to the supramolecular chemistry and self-assembly feature, if crystals are regarded as single chemical entities [3]. Self-assembly is based on complementary and explicit interactions between the building blocks in order to generate the final product [4].

The arrangement of the components in coordination polymers mostly only exist in the solid state [2]: the building blocks interact through coordination interactions and weaker forces such as hydrogen bonds, π–π stacking or van der Waals interactions in solution giving some small molecular units, and then, thanks to self-assembly processes coordination polymers grow based on the same interactions (Fig. 1) [5]. We can speak of reversible arrangements due to non-covalent bonds. Metal ions are generally called nodes whereas the ligands are the linkers.

The solid products are generally insoluble or degrade upon dissolution. Structures of coordination polymers can so far only be determined by X-ray crystallographic methods and characterizations in solution usually prove only the existence of oligomeric fragments.

1.1. Interests

The numerous literature contributions in the field of coordination polymers are due to several points:

- Incorporating metal ions in supramolecular networks allows to control metal atom positions in the final material, and adds properties to the material which are not only based alone on the metal ions, but also on the interplay between both binding partners. Types of metal centres and distances between them can be chosen so that stable functional solid materials can be tuned.

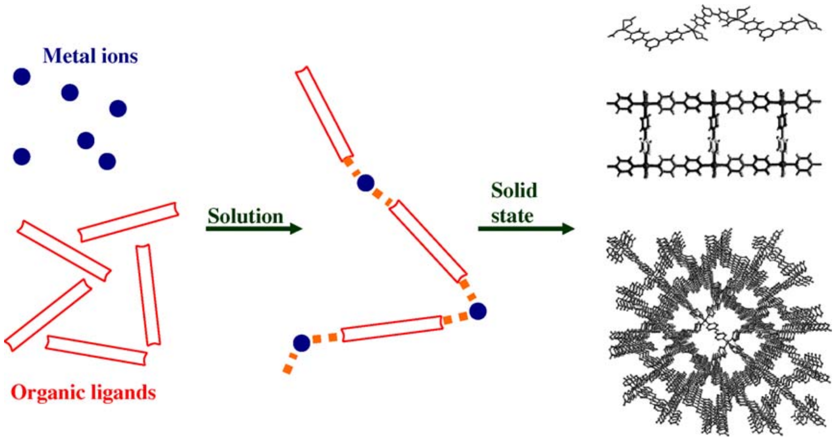


Fig. 1. Formation of coordination polymers. Adapted with permission from Refs. [6,7]. © 1999 Elsevier.

- The variety of “nodes and linkers” offers to the chemists infinite possibilities for building new species with intriguing architectures and topologies. Moreover, the studies of crystals become much easier thanks to the technological improvements in the field of X-ray measurements and computational resolution techniques.

1.2. Interactions

The process of building a coordination polymer is principally directed by the coordination bond. Coordination bonds are the donation of a lone electron pair of the ligand (Lewis base) to the metal cation (Lewis acid) and electrostatic attractions between the positively charged metal ion and a negatively polarized or charged donor atom of the ligand. The energy of such interactions is usually evaluated around 50 kJ mol^{-1} [8]. Weaker interactions also strongly influence the formation of coordination polymers. Most frequently encountered weak interactions are hereby shortly described.

Hydrogen bonds are defined by Steiner [9] as follows: *A D–H···A interaction is called a “hydrogen bond”, if* (1) *it constitutes a local bond* and (2) *D–H acts as proton donor to A*. For hydrogen bonds of weak to intermediate strengths, hydrogen bonds may be described with an “electrostatic plus van der Waals” model. For the strongest types of hydrogen bonds (rarely found in coordination polymers), their quasi-covalent nature has to be fully considered. Some systematic studies have been performed, with the use of structural database (especially the Cambridge Structural Database), in order to understand the strength and the directional preferences of hydrogen bonds [9–12]. The H···A distance should be, for instance, in the range 1.5–2.2 Å for strong O–H···O/N hydrogen bonds (with D–H···A angles in the range of 140–180°) and 2.0–3.0 Å for weak C–H···O/N contacts (with D–H···A angles in the range of 120–180°). The energy of such interactions varies from 15 to 40 kJ mol^{-1} for moderate hydrogen bonds.

π–π interactions can be of predominant importance during the coordination polymer formation. Janiak reviews this kind of interactions in metal complexes with aromatic nitrogen-containing ligands [13]. Aromatic–aromatic interactions involve face-to-face alignment (with or without offset) and edge-to-face orientations (C–H···π interactions). These interactions are based on the sum of several contributions (electrostatic, van der Waals interactions, repulsion and charge transfer), and the aromatic rings preferentially stack in an optimal way to minimize all the repulsive interaction components and maximize attraction. Geometrically important parameters are discussed in the corresponding review [13]. The investigation of the Cambridge Structural Database allows to determine the main parameters for π–π stacking in metal complexes with aromatic nitrogen-containing ligands [13]. For face-to-face interactions, the centroid–centroid distance is found between 3.4 and 3.8 Å (with an inclination angle between the two ring planes as small as possible) and an offset shift angle ranging between 16 and 40°. The energy of π–π interactions is estimated at 5–10 kJ mol^{-1}.

Metal–metal interactions based on d^{10} metal cations are controversely discussed, especially for silver cations, whereas they are more accepted for copper and gold cations. The energy of these bonds was roughly estimated to ca. 5 kJ mol^{-1} for, i.e. a silver–silver interaction [14].

Metal–aromatic interactions can be formed when metal cations accept π-electrons from unsaturated organic molecules. Geometrically important parameters are discussed in the corresponding review [8]. For instance for Ag^{I}, the main distances Ag–ring are ranged from 2.8 to 3.3 Å. The energy of metal–aromatic interactions is not well-known, but evaluated around 5–10 kJ mol^{-1}.

1.3. Synthetic methods

Four main synthetic strategies for obtaining coordination polymers are known from literature [5,15]. Improvement of synthesis is essential in order to get good quality single crystals suitable for X-ray measurement. It is important to remember that several processes with the same starting materials lead sometimes to different products: isomeric or polymorphic species will be discussed later.

Saturation methods allow the crystal formation from a mixture of the different reagents. Molecular recognition permits the construction of products following pre-determined rules. This technique needs convenient conditions:

- Crystals grow in saturated solutions. Ideal concentrations can be achieved by *slow evaporation* of the mother liquor.
- Solubility increases with temperature and crystals can appear during the *cooling* step, which has to be well-controlled as far as speed of cooling and final temperature are concerned.

Diffusion methods are preferred to get single crystals suitable for X-ray diffraction analysis instead of non- or poly-crystalline products, especially if the products are poorly soluble. The principle of this method is to slowly bring into contact the different species:

- One approach can be the *solvent liquid diffusion*: layers are formed; one contains the product in an adequate solvent, another is the precipitant solvent and both are separated with a solvent layer. The precipitant solvent slowly diffuses into the separate layer and crystal growth occurs at the interface.
- The other approach always concerning diffusion of compounds in solution is the *slow diffusion of reactants*. This technique is similar to the one before, the only difference is that the reactants are dissolved each separately in one of the two solutions; the separation between both solutions can be a solution layer and/or physical barriers. Instead of liquid solvents, gels are also used as diffusion and crystallization media in some cases, especially to slow down diffusion and to avoid precipitation of bulk material.

Hydro(solvo)thermal methods are originally used for the synthesis of zeolithes, but have been adopted to the formation of coordination polymers. They exploit the self-assembly of products from soluble precursors. The running temperature range is usually 120–260 °C inside a closed space (autoclave) under autogenous pressure. Under these conditions the reduced viscosity of water enhances the diffusion process and thus extraction of solids and crystal growth from solution are favoured. As the difference of solubility between organic and inorganic components in the same solvent is often a barrier in the formation of single crystals, hydrothermal experiments can be a good alternative as solubilities of starting materials can be increased. This crystallization technique is a non-equilibrium synthesis and may lead to metastable products. This can be influenced mainly by the cooling speed at the end of the reaction.

Microwave and ultrasonic methods are so far less used methods for the coordination polymer formation. These methods are also based on the improvement of solubilities in order to better react or crystallize the involved species and products. They remain to be exploited more efficiently.

2. Overview on the diversity of coordination polymers

2.1. Building blocks

There are four different kinds of building bricks used for the construction of infinite metal-organic frameworks, crucially influencing on the final properties of the compound.

Organic ligands act as bridging organic groups between the metal ions. Typical organic ligand molecules are shown on Fig. 2. For possible infinite expansion, ligand molecules have to be multidentate with at least two donor atoms, mostly N-, O- or S-donors. Ligand molecules may differ from each other in their charges: most used ligands are neutral or anionic. Another structure determining factor is the “body” of the organic ligands: their shapes (rigid or not); their lengths (distance between the coordination functions) and their functionalities (further presence of heteroatoms, aromatic rings, alkyl chains, . . .). Finally, the ligand molecules can be symmetric, chiral or not, i.e. combining different functionalities on the same molecule.

Metal ions are involved in the structure depending on their size, hardness/softness, ligand-field stabilization energy and coordination geometries (linear, trigonal-planar, T-shaped, tetrahedral, square-planar, square-pyramidal, octahedral, trigonal-prismatic, pentagonal-bipyramidal or trigonal-bipyramidal). Different kind of metal atoms have been studied, for instance transition metal ions, lanthanide ions.

- *Transition metal ions* are most widely used: choosing one or another metal element means choosing the coordination geometry, i.e. the node shape, as well as choosing the potentially required properties of the future materials. Ag^I and Cu^I ions have a d^{10} electronic configuration and thus are more “flexible”: their coordination sphere can change depending on the synthesis conditions. Thus Ag^I is found in a wide range of coordination environments: linear, trigonal, tetrahedral, square-planar, square-pyramidal and octahedral; for Cu^I, it is usually tetrahedral or trigonal. The transition metals with other electronic configurations have defined coordination environments, for instance, Ni^{II} is preferentially tetra-coordinated and mainly square planar, Cu^{II} usually has Jahn–Teller distorted octahedral coordination geometry (and eventually square-planar or square-pyramidal), Co^{II} an octahedral geometry and Pt^{II} a square-planar geometry, so that a large number of combinations are in principle possible.
- *Lanthanide ions* are less used because of the high flexibility of their coordination environments which makes their behaviour difficult to predict in the presence of simple donor ligands. Their coordination numbers can vary from 7 to 10. However, with these connectors, some original topologies can be formed and particular applications become conceivable.

Counter ions are present in the structure when neutral ligands are used. They can influence the metal ion environment (more or less coordinating counter ions) but also the overall structure, being involved in weak interactions or acting as guest molecules in void spaces in the solid state.

Solvent molecules may co-crystallize, increasing the number of possible weak interactions in the final solid state packing, and can also act as guest molecules in the vacant space between the polymer construct. They may play a crucial role when it comes to the construction of highly porous materials. As nature usually avoids large empty spaces, solvent molecules may come in a first synthetic step as space fillers which can be removed once the final network is formed and stabilized in the solid state.

2.2. Dimensionality and motifs

The organisation of the building blocks together can lead to metal-organic frameworks of different dimensionalities: one-, two- or three-dimensional architectures. Fig. 3 represents the simplest ways of organisation in order to construct these three principal architecture types. Linear organic ligands with two donors systems (D) and the spacer (S) are here schematized and only the coordination interactions are considered. Dimensionality is often determined by the nodes (metal centres): in one-dimensional motifs the metal ion is coordinated with two ligand molecules, metal ions and organic ligands alternate “infinitely”, leading to a chain; two-dimensional compounds are obtained with three or four ligand molecules coordinating around the metal ion and the elementary motif expands now in two directions; with metal ions of higher coordination number (tetrahedral or octahedral nodes), three-dimensional structures can be built.

Obviously, the elementary units are not always so simple and there are a lot of one-, two- or three-dimensional architectural types depending on the building blocks and the experimental conditions. These architectures can be schematized only using nodes and links. Figs. 4–6 [5] represent, respectively, some of the most important known motifs. Along this review, we will often discuss and refer to these network motifs.

One other important feature concerning the analyses of coordination polymers architectures is the interpenetration, in which two- or three-dimensional motifs are interweaving [16]. Some examples are shown on Fig. 7.

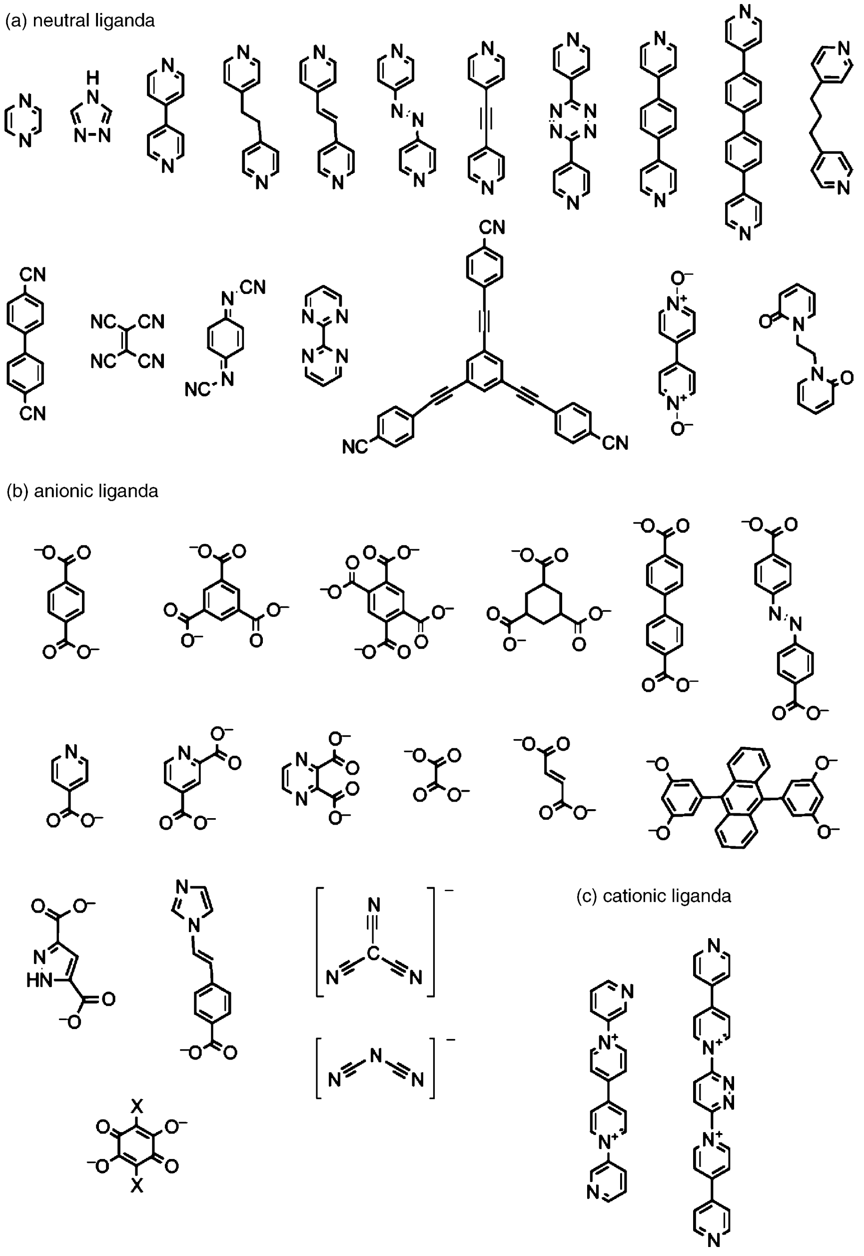


Fig. 2. Typical used organic molecules as organic linkers in coordination polymers. Reprinted with permission from Ref [5]. © 2004 Elsevier.

Considering the huge choice of possible building units, one can easily imagine the diversity of new synthesizable materials. In order to illustrate the wide diversity of related coordination polymers, some examples of metal-organic frameworks will be presented; the aim of the following paragraphs is not to make an exhaustive list but only to present an overview of the coordination polymer features. They are classified along their dimensionalities. The shown motifs are the most typical ones and are based on coordination interactions between ligand molecules and metal ions. It is clear that other interactions play also an important role during the formation of the crystals, but the definition of the final compounds dimensionality is based on the metal complexation. Due to the abundance of known metal-organic systems, we will only report the systems containing one type of ligand and one type of metal ions.

2.3. *One-dimensional motifs*

2.3.1. *Linear chains*

The mind will implicitly associate one-dimensional motifs with *linear chains*, like a regular bicolour necklace. This simplest one-dimensional motif exists obviously.

For instance, crystals of $\{[Co(H_2O)_4(pyrazine)](NO_3)_2\cdot 2H_2O\}_n$ appear from a heated mixture of pyrazine in acetonitrile and $Co(NO_3)_2\cdot 6H_2O$ in ethanol [17]. They show a one-dimensional linear chain structure alternating pyrazine molecules and $Co(H_2O)_4$ units (Fig. 8). Cobalt atoms are hexacoordinated, the oxygen atoms of the four coordinated water molecules occupying the equatorial positions and the nitrogen atoms of two different ligand molecules the axial positions. This arrangement is due to the coordination site occupation of the

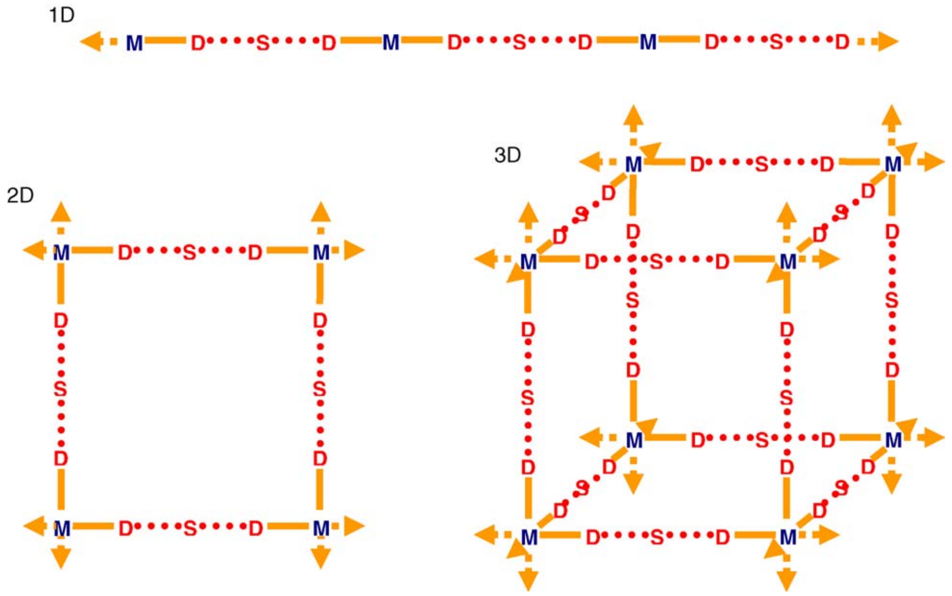


Fig. 3. Dimensionality of the metal-organic frameworks (M, metal ions; D, donor groups of the ligand; S, spacer inside the ligand) Adapted with permission from Ref. [2]. © 2003 The Royal Society of Chemistry.

hexa-coordinating metal ions (*trans*-arrangement of two different ligand molecules in axial positions, and the equatorial positions occupied with counter anions or solvent molecules) and to the fact that the ligand is linear and symmetric.

We can observe analogous arrangements in $\{[Ni(C_{12}H_{30}N_6O_2)(C_8H_4O_4)]\cdot4H_2O\}_n$ [18] where the ligand molecule is the stiff terephthalate dianion and the equatorial positions are occupied by a macrocycle (Fig. 9). Linear chains can also be realized with less rigid, even flexible ligands such as the ethanediyl bis(isonicotinate) (=L_1) used by Fromm and co-workers in combination with copper(I) chloride (Fig. 10) [19], or in $\{[Mn(C_{12}N_2H_{10})(NCS)_2(CH_3OH)_2]\}_n$ [20] in which Mn^{II} is coordinated by two *trans*-1,2-bis(4-pyridyl)ethane ligands, two isothiocyanate ions and two methanol molecules.

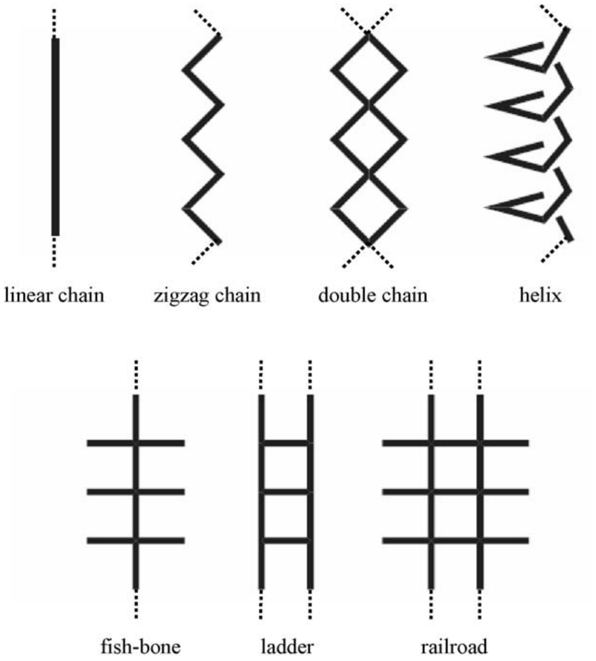


Fig. 4. 1D coordination polymer motifs. Adapted with permission from Ref. [5]. © 2004 Elsevier.

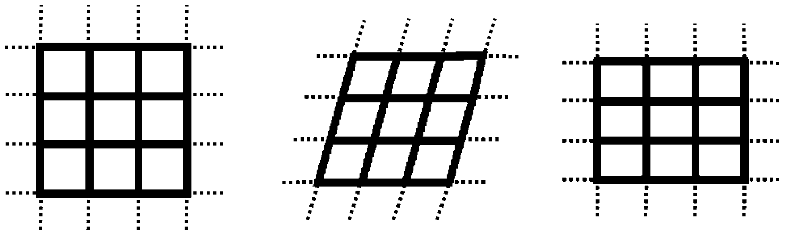
Some other linear chain motifs can be achieved by a more original organisation of the ligand molecules with the metal ions. The compound $\{[Cu_3(cpida)_2(H_2O)_4]\cdot4H_2O\}_n$ [21], for instance, shows deprotonated *N*-(4-carboxyphenyl)iminodiacetic acid (H_3cpida) molecules alternating with Cu^{II} units (Fig. 11).

Although the one-dimensional chain organisation seems to be simple, there are many possible permutations in the packing, taking into account the interactions during the crystal formation. Janiak and co-workers have reported two one-dimensional chains based on terephthalate dianions: $\{[M(\mu\text{-}C_{12}H_{30}N_6O_2)(NH_3)_2]\}_n$ ($M = Cu^{II}$, Cd^{II}) obtained by slow evaporation [22]. While the two systems seem to be similar, they differ from the coordination sphere of the cations. In the copper compound, Cu^{II} (Fig. 12a and b) is square-planar coordinated by two ammonia and two ligand molecules in a monodentate way, leading to a *trans*-arrangement of the ligand molecules and linear chains, whereas in the second compound the ligand acts as a bidentate pincer (Fig. 12c and d). The Cd^{II} ion is thus coordinated with six atoms in a trigonal-prismatic way; the ammonia molecules are in *cis*-position on one side of the cadmium ion, and the ligand molecules occupy the other side. Some *zig–zag chains* are thus formed in this second case due to the difference in the coordination orientations of the two metal ions.

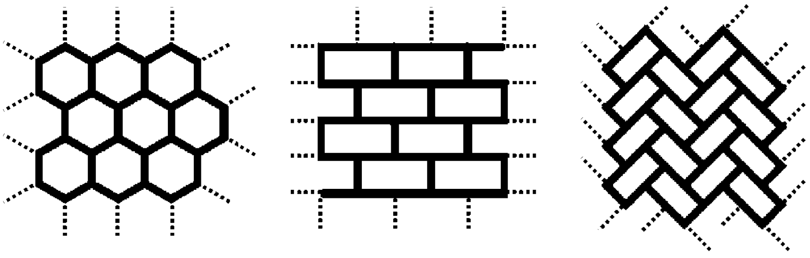
A similar arrangement of cadmium cations with terephthalate dianions as connecting ligands is reported by Qiu and co-workers [23] with phenantroline molecules instead of ammonia ones.

2.3.2. *Zig–zag chains*

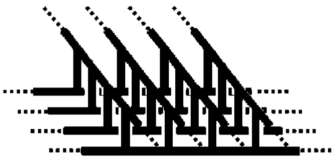
The formation of zig–zag chains can also be induced by the shape of the ligand molecules. A first simple example will rationalize this fact: in comparison of the coordination poly-



square grid rhombic grid rectangular grid



honeycomb grid brick wall herringbone



bilayer (tongue-and-groove etc.)

Fig. 5. 2D coordination polymer motifs. Adapted with permission from Ref. [5]. © 2004 Elsevier.

mers obtained from $Cu(HCO_2)_2{\cdot}yH_2O$ and pyrazine (pyz) or pyrimidine (pym) [24]. The difference of these two ligands is the relative position of the two N-donor atoms on the ring. As shown on Fig. 13 pyrazine ligand molecules lead to linear chains whereas zig–zag chains occur by use of pyrimidine ligand molecules.

This second example shows the similar influence of the position of the two N-donor atoms on the ring. Under similar experimental conditions acetylene-bridged *N*,*N*′-bidentate ligands with different positions of the nitrogen atoms on the rings (*N*,*N*′-dpa) coordinate with cobalt ions. The coordination polymer containing 3,3′-dpa shows a zig–zag chain motif (Fig. 14a), whereas the compound with 4,4′-dpa shows a one-dimensional ladder-like organisation, which is yet another form of a one-dimensional structure (Fig. 14b) [25,26].

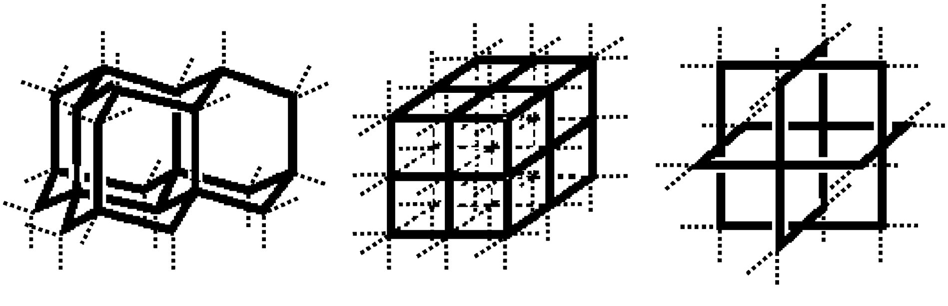
Comparable zig–zag chains can be also obtained with longer bent ligand molecules or with flexible ligand molecules. The coordination polymer $\{[Cu(dtmp)(dmf)Cl_2]dmf\}_n$ (dtmp = 1,6-di(triazole-1-yl-methyl)-4-methylphenol) self-assembles in the reaction mixture and shows a zig–zag chain motif (Fig. 15) [27]. The flexibility of the ligand allows its *cis* conformation. Cu^{II} ions are five coordinated with two nitrogen atoms of two different ligand molecules, two terminal chloride anions and one oxygen atom of the coordinated dmf molecules.

A solution of 2,2′-bis(4-pyridylmethyleneoxy)-1,1′-biphenylene (4,4′-bpp) in methanol diffuses into an aqueous solution of $ZnCl_2$ or $ZnBr_2$ in order to lead to crystals showing zig–zag chains: the Zn atoms are tetra-coordinated with two different bent ligand molecules and with two terminal halide atoms as shown on Fig. 16 [28].

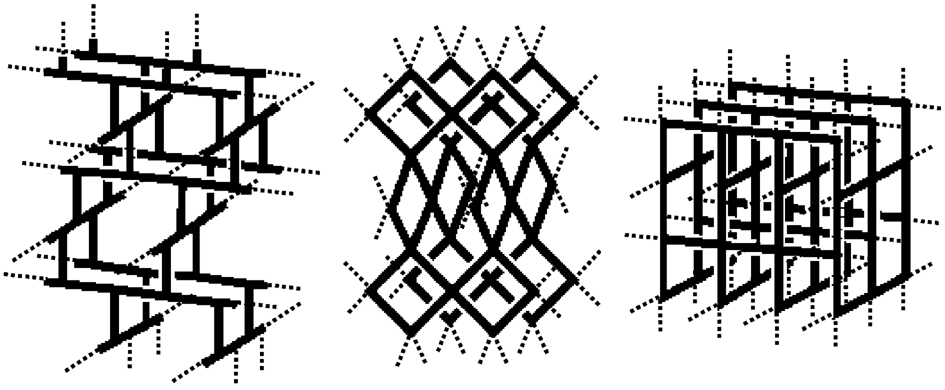
2.3.3. Double chains

From a high-dilution synthesis, crystals of $\{[Cu(2,3\text{-}pydcH)_2]\}_n$ are obtained [29]. The ligand 2,3-pyridine dicarboxylic acid (2,3-$pydcH_2$) is a bidentate asymmetric molecule. The repeating units of this coordination polymer are metallacycles: two ligand molecules bridge two closest copper atoms in the chain (Fig. 17). Each Cu^{II} atom has a distorted octahedral coordination sphere; the apical positions are occupied by the oxygen atoms of the non-deprotonated 3-carboxyl groups; the equatorial ones with two nitrogen atoms and two oxygen atoms of the deprotonated 2-carboxyl groups. This motif is called a *double chain* motif.

Recrystallization of Zn^{II} salts and 4,4′-dipyridyl disulfide (4pds) coordination polymers in different solvents leads to double chain structural motifs [30]. Zn^{II} is hexa-coordinated and the equatorial positions are occupied with four nitrogen atoms of four different ligand molecules and the apical ones with counter anions or solvent molecules. The repeating unit is a Zn_2L_2 ring. Fig. 18 shows, for instance, the compound $\{[Zn(SCN)_2(4pds)_2](dmf)_2\}_n$. The torsion angle C–S–S–C is of ca. 90°, thus the bend shape of the ligand molecules explains

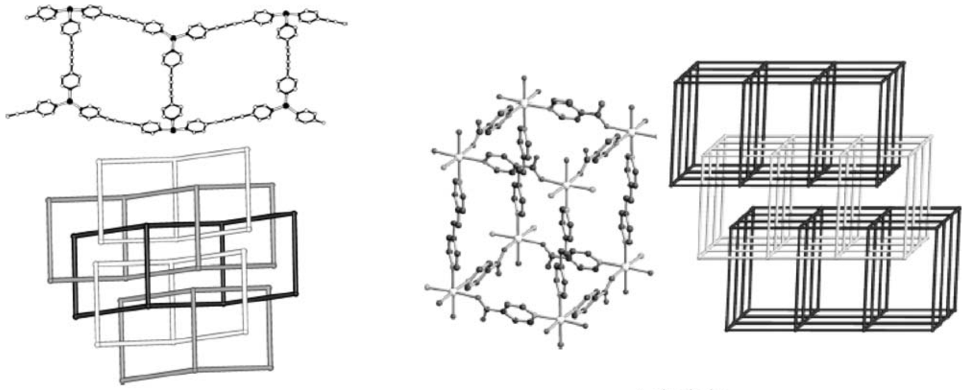


diamondoïd net octahedral net NbO net



$ThSi_2$ net PtS net $CdSO_4$ net

Fig. 6. 3D coordination polymer motifs. Adapted with permission from Ref. [5]. © 2004 Elsevier.



A single undulated layer
and the (1D → 2D) catenation in
$\{[Cu_2(CH_3CN)_2L_3](PF_6)_2\}_n$
L = 1,4-bis(4-pyridyl)butadiyne

A single box
and the catenation of the double layers in
$\{[Cd(in)_2(bpe)_{1/2}(H_2O)]\}_n$
in = isonicotinate
L = 1,2-bis(4-pyridyl)ethane

Fig. 7. Two examples of interpenetrated systems. Reprinted with permission from Ref. [16]. © 2003 Elsevier.

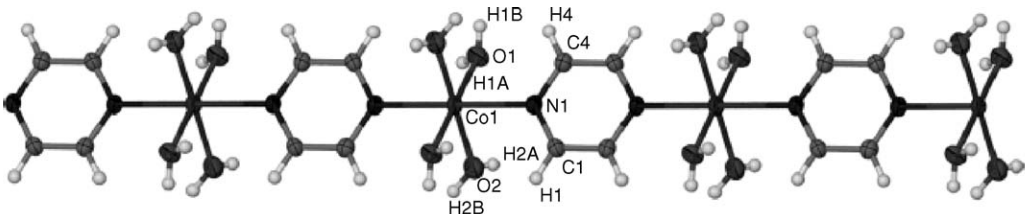


Fig. 8. One-dimensional polymer chain of $\{[Co(H_2O)_4(pyrazine)](NO_3)_2{\cdot}2H_2O\}_n$. Reprinted with permission from Ref. [17]. © 2005 Elsevier.

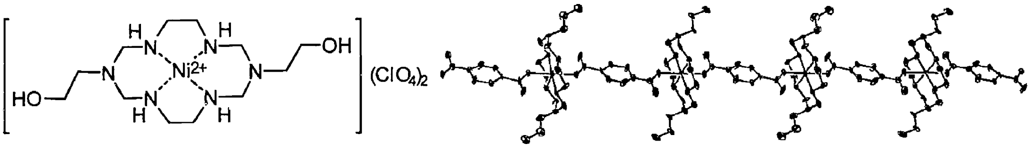


Fig. 9. The one-dimensional polymer: $\{[Ni(C_{12}H_{30}N_6O_2)(C_8H_4O_4)]\cdot 4H_2O\}_n$. Reprinted with permission from Ref. [18]. © 1999 American Chemical Society.

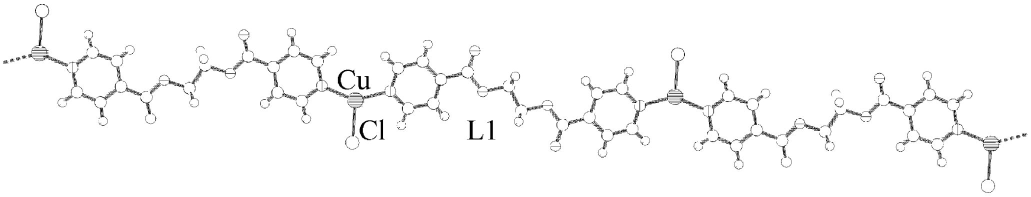


Fig. 10. Coordination mode of Cu^I in $[Cu(L_1)(Cl)]_n$ (L_1 = ethanediyl bis(isonicotinate)). Reprinted with permission from Ref. [19]. © 2003 The Royal Society of Chemistry.

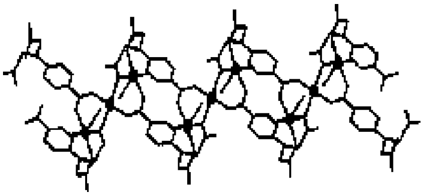


Fig. 11. One-dimensional motif in $\{[Cu_3(cpida)_2(H_2O)_4]\cdot 4H_2O\}_n$ (copper atoms are represented with black circles, H_3cpida = *N*-(4-carboxyphenyl)iminodiacetic acid). Reprinted with permission from Ref. [21]. © 2004 Wiley–VCH Verlag.

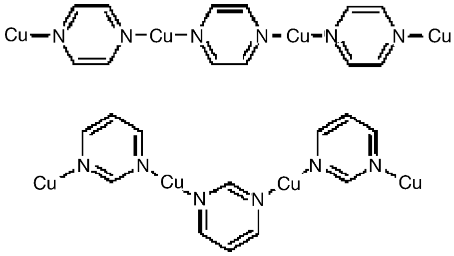


Fig. 13. Schematic representation of the skeleton of one-dimensional coordination polymers: $\{[Cu(L_2)(HCO_2)_2]\}_n$ (L_2 = pyrazine or pyrimidine). Reprinted with permission from Ref. [24]. © 2005 American Chemical Society.

the rhombohedral chains. In this series of Zn^{II} coordination polymers derived from 4dps ligands, an important additional feature appears, as the ligand can adopt two forms of enantiomers. The double chains can be achiral or chiral.

Double chain motifs can also be found in compounds based on polydentate ligand molecules. 1,2,7,8-Benzenetetracarboxylic acid molecules (H_4bta) self-assemble with Mn^{II} ions in presence of 4,4′-bipyridine (bpy) in a basic solution affording crystals with a double chain structural motif (Fig. 19). The Hbta molecules act as tridentate ligand molecules on an octahedral Mn^{II} ion, the coordination sphere of Mn^{II} ion being completed with two water molecules and one Hbyp molecule [31]. Double chain motifs can also appear with flexi-

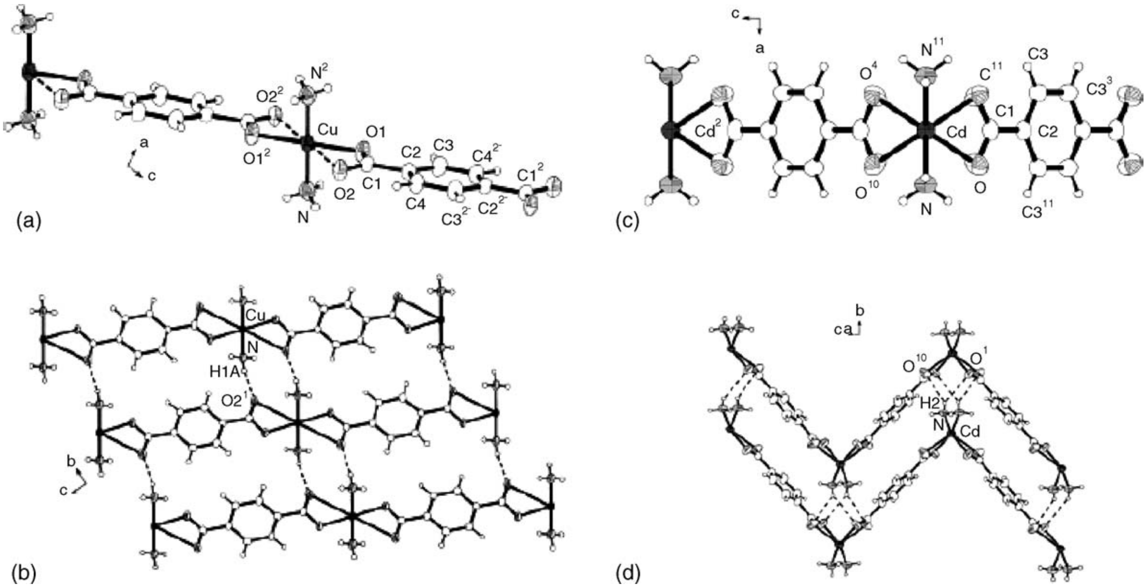


Fig. 12. (a and b) $\{[Cu(\mu\text{-}C_{12}H_{30}N_6O_2)(NH_3)_2]\}_n$ and (c and d) $\{[Cd(\mu\text{-}C_{12}H_{30}N_6O_2)(NH_3)_2]\}_n$. Reprinted with permission from Ref. [22]. © 2004 Wiley–VCH Verlag.

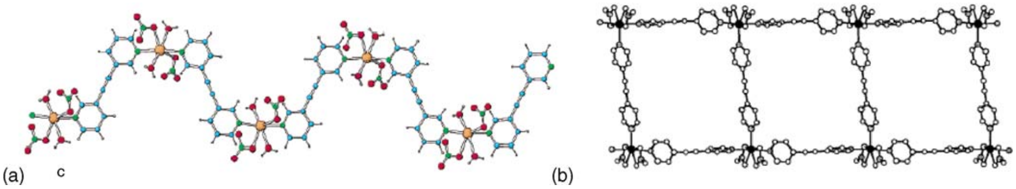


Fig. 14. (a) $\{[Cd(3,3'\text{-dpa})(NO_3)_2(H_2O)_2]\}_n$ and (b) $\{[Cd(NO_3)_2(4,4'\text{-dpa})_{1.5}]\}_n$. Reprinted with permission from Refs. [25,26]. © 2002 American Chemical Society.

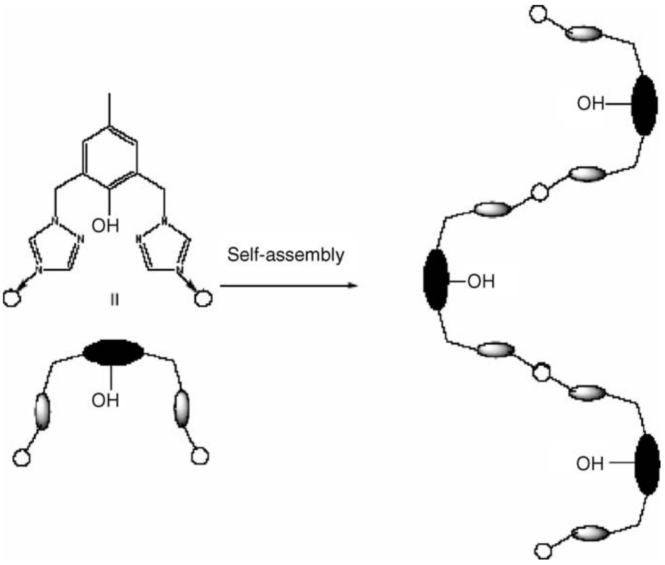


Fig. 15. Zig–zag coordination polymers $\{[Cu(dtmp)(dmf)Cl_2]dmf\}_n$ (dtmp = 1,6-di(triazole-1-yl-methyl)-4-methylphenol). Reprinted with permission from Ref. [27]. © 2004 Elsevier.

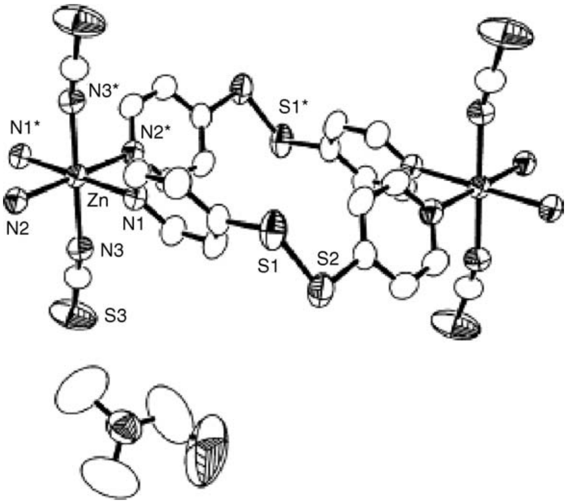


Fig. 18. The loop Zn_2L_2 in $\{[Zn(SCN)_2(4pds)_2](dmf)_2\}_n$ (4dps = 4,4′-dipyridyl disulfide). Reprinted with permission from Ref. [30]. © 2005 American Chemical Society.

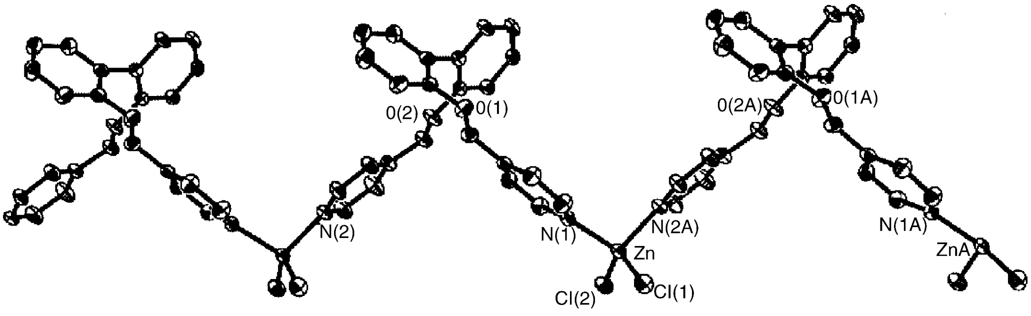


Fig. 16. One-dimensional polymeric chain of $\{[Zn(4,4'\text{-bpp})Br_2]\}_n$ (4,4′-bpp = 2,2′-bis(4-pyridylmethyleneoxy)-1,1′-biphenylene). Reprinted with permission from Ref. [28]. © 2004 Wiley–VCH Verlag.

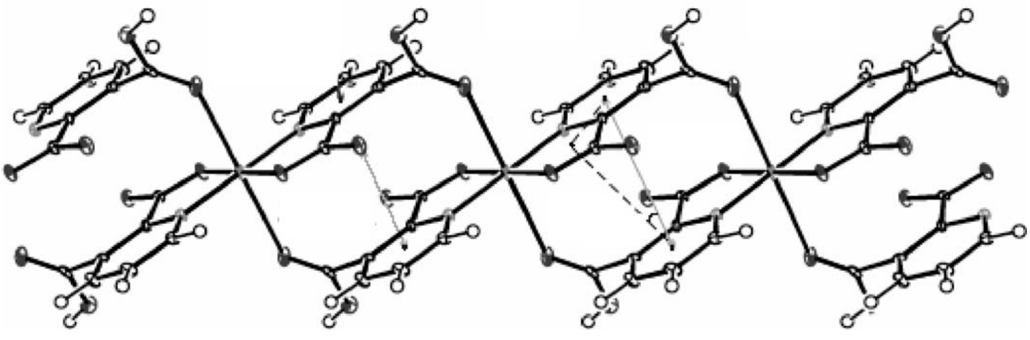


Fig. 17. Double chain motif in $\{[Cu(2,3\text{-pydcH})_2]\}_n$ (2,3-pydcH$_2$ = 2,3-pyridine dicarboxylic acid). Reprinted with permission from Ref. [29]. © 2003 Elsevier.

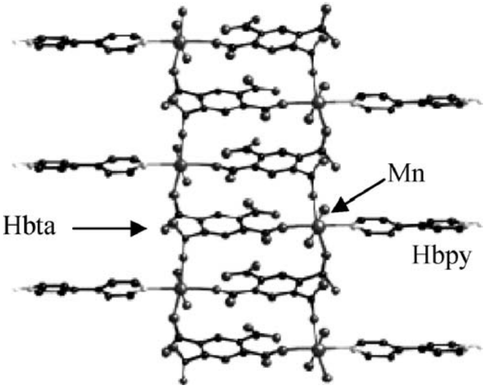


Fig. 19. Double chain motif in $\{[Mn(Hbta)(Hbyp)(H_2O)_2]\}_n$ (H_4bta = 1,2,7,8-benzenetetracarboxylic acid). Reprinted with permission from Ref. [31]. © 2004 Wiley–VCH Verlag.

ble or well-shaped ligand molecules in association with a large variety of metal centers.

2.3.4. Ladder-like

Ladder-like one-dimensional motifs can also be formed. An example is shown on Fig. 14b. The hepta-coordinated cadmium ions are coordinated with three different ligand molecules leading to a “T-shape” organisation of the ligand molecules around the metal center; the other sites of the coordination sphere are blocked with the counter anions avoiding the extension of the structure in further direction. Another ladder-like organisation is found in the compound $\{[Cu(2,3\text{-dimethylpyrazine})Br_2]\}_n$ [32]. This compound co-crystallizes as main product of the slow diffusion between methanolic solutions of the ligand and $CuBr_2$. In this case two “rails” formed by bridging 2,3-dimethylpyrazine between the Cu^{II} ions are linked together by bridging bromide ions (Fig. 20). The additional bromide anions are terminal ones.

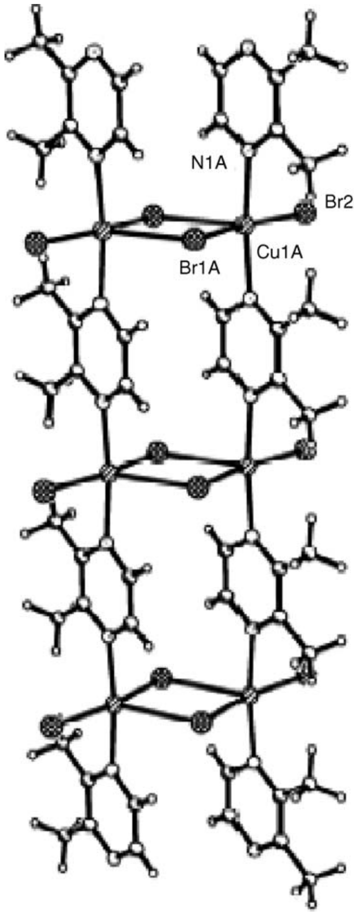


Fig. 20. Ladder-like arrangement in the compound $\{[Cu(2,3\text{-dimethylpyrazine})Br_2]\}_n$. Reprinted with permission from Ref. [32]. © 2005 Elsevier.

2.3.5. Helix

The least common one-dimensional motif is the *helical chain*. $\{[HgBr_2(2,5\text{-bis(3-pyridyl)-1,3,4-oxadiazole})]\}_n$ crystals appear after the slow diffusion of the ligand solution in methanol into an aqueous solution of $HgBr_2$ [33]. The Hg^{II} has a distorted tetrahedral environment consisting of two nitrogen atoms of two ligand molecules and of two terminal bromide atoms. The $HgBr_2$ and the ligand units alternate in order to form a one-dimensional chain. The bent shape of the ligand molecules and its coordination at the Hg^{II} centers give a helical twist to the chain (Fig. 21). In comparison, the coordination polymer obtained with HgI_2 and the similar 2,5-bis(4-pyridyl)-1,3,4-oxadiazole ligand (except for the position of the nitrogen atoms on the ring) shows a one-dimensional zig–zag motif, as the ligand coordination orientation is different. Some other examples of helical chains can be found [34,35], for instance, the anion bis[3-(2-pyridyl)pyrazol-1-yl)]phosphinate crystallizes with Ag^I or Tl^I in order to form helical strands (Fig. 22) [36]; the complex $\{[Ag(N,N'\text{-di(2-pyridyl)oxamide})]NO_3\}_n$ crystallizes also in single-twist helices [37].

Some few double helical motifs are related, especially if there are several kinds of donor groups in the ligand molecule or with flexible ligands. For instance, the ligand 1,3-bis(4-pyridyl)propane (bpp) reacts with $AgCF_3SO_3$ by diffusion technique [38]. The structure of the resulting product shows double helical chains, as one-dimensional chains are intertwined. The contacts between the two chains are Ag–Ag interactions and π-stacking as shown on Fig. 23.

In the one-dimensional chain motif, ligand and node centers alternate in one direction so that the repeating unit is formed with one node and one ligand and the proportion metal to ligand is 1:1 (except for the double chain motifs).

2.4. Two-dimensional motifs

2.4.1. Square grid

Square grid networks are the simplest example of the two-dimensional motifs. In these coordination polymers the proportion metal to ligand usually is 1:2. The metal centers are coordinated with four different ligand molecules and the repetition of this unit allows the propagation of the structure in two dimensions.

The ligand 1,4-bis(imidazol-1-ylmethyl)benzene (bix) reacts with Mn^{II} ions in order to form single crystals in which the

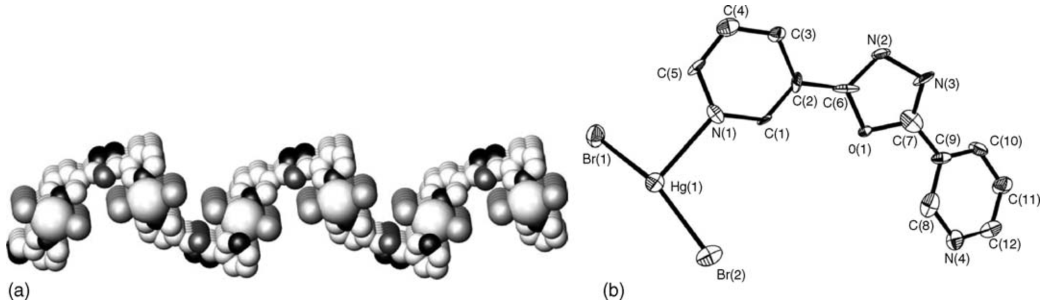


Fig. 21. $\{[HgBr_2(2,5\text{-bis}(3\text{-pyridyl})\text{-}1,3,4\text{-oxadiazole})]\}_n$: (a) helical chain and (b) coordination of Hg^{II} and shape of the ligand. Reprinted with permission from Ref. [33]. © 2005 Elsevier.

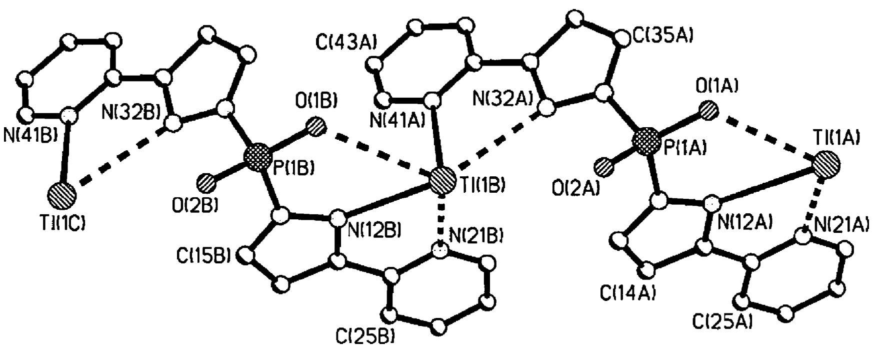


Fig. 22. Crystal structure of the one-dimensional helical chain of $\{[Tl(bis[3\text{-}(2\text{-pyridyl})pyrazol\text{-}1\text{-yl})]phosphinate)]\cdot MeOH\}_n$. Reprinted with permission from Ref. [36]. © 1997 The Royal Society of Chemistry.

motifs are perfect square grid layers (Fig. 24) [39]. The metal ions have an octahedral environment: the equatorial positions are occupied by the nitrogen atoms of four ligand molecules and the apical ones by the counter anions (azide or dicyanamide anions). A similar example affords a square grid motif [40]: the metal node is an Uranyl^{VI} ion and the bridging ligand is 1-oxo-4-pyridylcarboxylate (opyca). Single crystals appear during the hydrolysis reaction of $UO_2(NO_3)_2$ with the 1-oxo-4-cyanopyridine under hydrothermal conditions (Fig. 25).

A lot of two-dimensional networks based on square grid motifs can be found in the literature, but also a lot of derived motifs such as *rhombic* or *rectangular grids* [40–43]. In these cases, the metal centers are also linked with four ligand molecules.

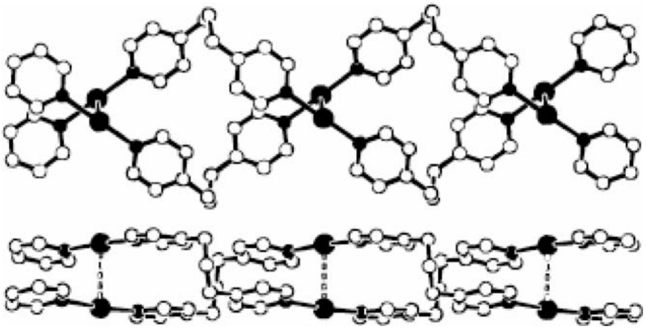


Fig. 23. Double helical motif in the compound $\{[Ag(bpp)](CF_3SO_3)\}_n$ (bpp = 1,3-bis(4-pyridyl)propane). Reprinted with permission from Ref. [38]. © 1997 American Chemical Society.

2.4.2. 2D-motifs with T-shape nodes

If the metal ions are only coordinated with three ligand molecules giving a “T-shape” around the node, layers are formed and the motifs are called *honeycomb grid*, *brick wall*, *herringbone* motifs or other *parquet floor* architectures. Some of these motifs are shown by Necas and co-workers [44] with coor-

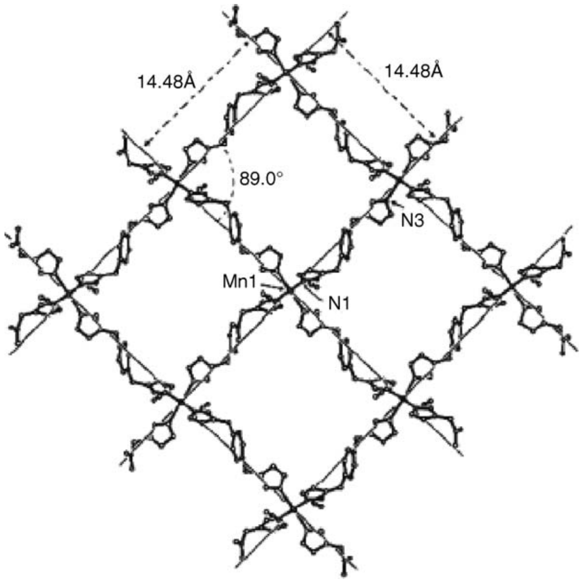


Fig. 24. Square grid network in $\{[Mn(N_3)_2(bix)_2]\}_n$ (bix = 1,4-bis(imidazol-1-ylmethyl)benzene (bix)). Reprinted with permission from Ref. [39]. © 2004 The Royal Society of Chemistry.

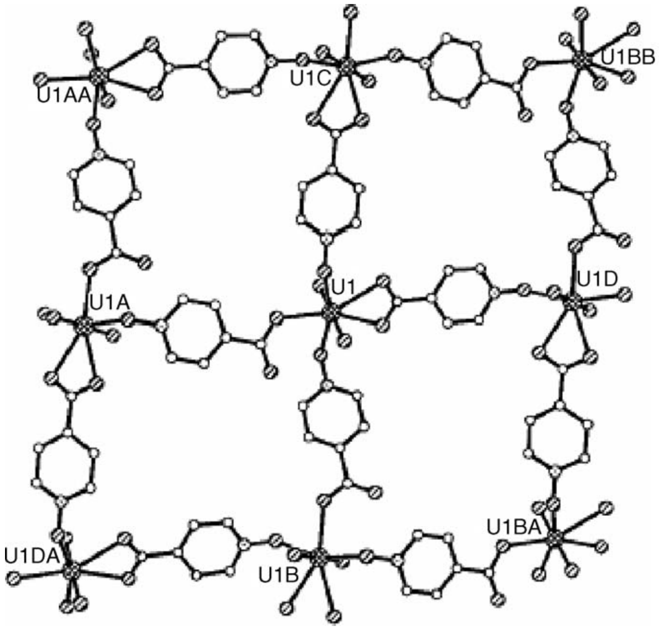


Fig. 25. 2D square grid motif in $\{[UO_2(opyca)_2]\}_n$ (opyca = 1-oxo-4-pyridylcarboxylate). Reprinted with permission from Ref. [40]. © 2003 Wiley–VCH Verlag.

dination polymers containing lanthanide ions and the ligand $Ph_2P(O)\text{-}CH_2CH_2\text{-}P(O)Ph_2$ ($dppeO_2$) (Fig. 26). In these cases the proportion metal-to-ligand is 1:1.5. To generate “T-shaped” connectors, some coordination sites of the metal center have to be blocked by highly coordinating counter anions such as halide anions or sometimes nitrate anions or by additional terminal ligand molecules.

Another motif containing “T-shaped” metal centers is the *bilayer* one. $\{[Cu(bpy)_{2.5}(H_2O)](ClO_4)_2\cdot(H_2O)\cdot(CH_3OH)_{1.5}\}_n$ presents this structural motif [45] (bpy = 4,4′-bipyridine). Each Cu^{II} center has a distorted square-planar geometry surrounded by four nitrogen atoms in the equatorial positions: three of the bidentate bridging bipyridine molecules and one of the monodentate terminal ligand connector, the apical coordination sites being occupied with weakly coordinated water molecules (Fig. 27). The proportion metal-to-ligand is now 1:2.5.

Thus, the two-dimensional structures are reached when three or four ligand molecules act as connectors between the node centers. The potential remaining coordination sites of the centers are occupied with other (terminal) building blocks (counter-anions, solvent molecules or additional organic molecules). The proportions metal to ligand are no more 1:1 as in the one-dimensional networks (except for double chain motifs), but $ML_{1.5}$, ML_2 or $ML_{2.5}$. A large variety of nodes can be found in such complexes. These kinds of constructions can show cavities. This remaining space is usually filled with guest molecules (counter ions or solvent molecules), by adequate stacking of the sheets or thanks to interpenetration.

2.5. *Three-dimensional motifs*

It is relatively easy to imagine now the requirements necessary to build three-dimensional complexes. The extension has to occur in the tree dimensions from the nodes and through the ligand connectors. The geometry of such compounds can be more complex.

2.5.1. *Diamondoid net*

One of the well-known and frequently found three-dimensional motifs is the *diamondoid* network. Each node is connected to four bridging ligands in a tetrahedral way, leading to a three-dimensional diamond-like network. This motif can be found in the structure obtained from Cd^{II} ions as nodes and the dicarboxylate 3,3′-azodibenzoate (3,3′-azdb) as connec-

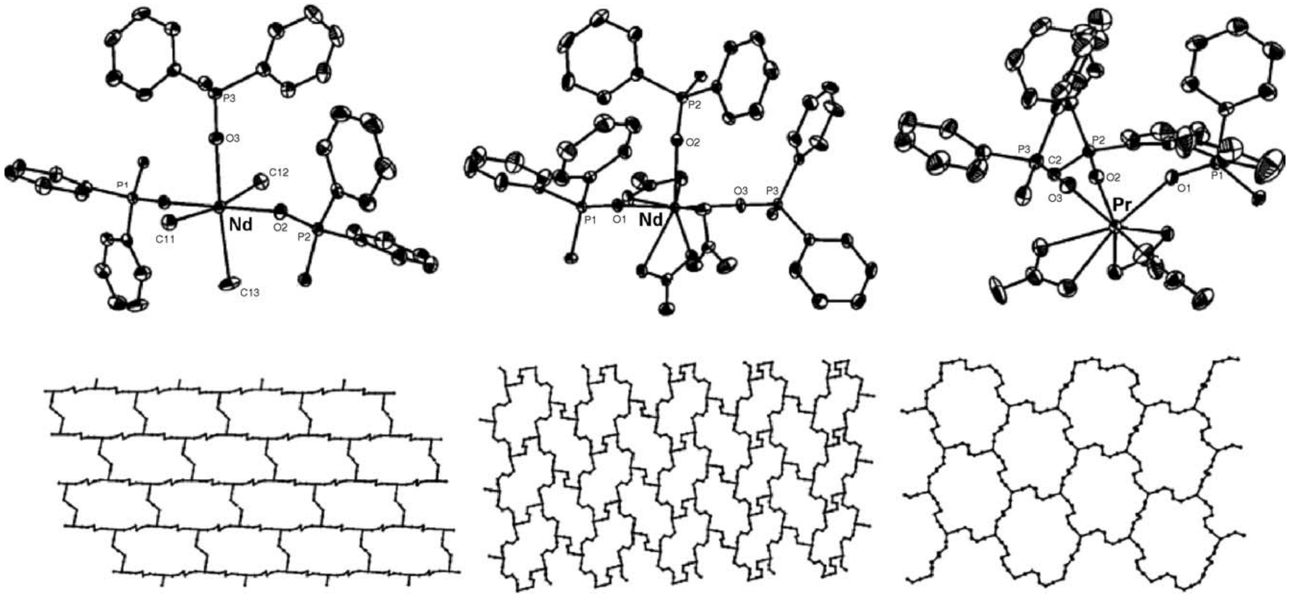


Fig. 26. From left to right: brick wall motif in $\{[NdCl_3(dppeO_2)_{1.5}]\}_n$; parquet floor motif in $\{[Nd(NO_3)_3(dppeO_2)_{1.5}]\}_n$ and pseudo-honeycomb motif in $\{[Pr(NO_3)_3(dppeO_2)_{1.5}]\}_n$ ($dppeO_2 = Ph_2P(O)\text{-}CH_2CH_2\text{-}P(O)Ph_2$). Reprinted with permission from Ref. [44]. © 2005 American Chemical Society.

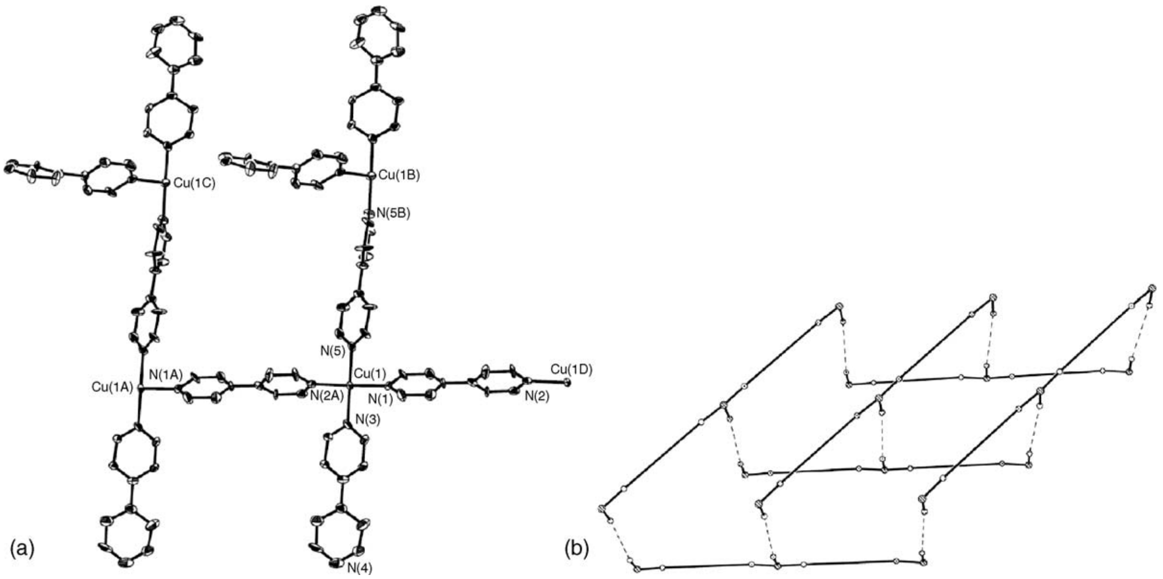


Fig. 27. Bilayer structural motif in $\{[Cu(bpy)_{2.5}(H_2O)](ClO_4)_2\cdot(H_2O)\cdot(CH_3OH)_{1.5}\}_n$ (water, perchlorate and methanol molecules are omitted for clarity; bpy = 4,4′-bipyridine): (a) coordination mode of the Cu^{II} ion; (b) bilayer architecture (terminal ligands are omitted, solid lines, “chain makers”; dashed lines, “linker between the chains” symbolized the bridging ligands and black circles the Cu^{II} centers). Reprinted with permission from Ref. [45]. © 2004 Elsevier.

tors [46]. The cadmium ions are eight-coordinate but they act as four-connecting nodes, as the carboxylate groups are bidentate. On Fig. 28, it can be noted that this arrangement creates large cavities due to the size of the ligand (in this case, the average distances between the cadmium atoms are 15 Å inside a cavity). When the intraframework voids are relatively large, interpenetration of a network by other independent networks is a common phenomenon. The degree of interpenetration depends on the length of the cavity’s edge, i.e. of the ligand molecule. In this structure, six independent interwoven diamondoid networks coexist (Fig. 28).

Examples affording this motif are numerous. Lin’s group relates two examples of diamondoid structures formed of Zn^{II} or Cd^{II} ions linked by the asymmetric ligand (4-[2-(4-pyridyl)ethenyl]benzoate = L_3) [47]. The metal ions have a distorted octahedral or tetrahedral environment so that the diamondoid structure can appear. In this case, the number of interpenetration is eight (Fig. 29).

This motif is sometimes distorted in correlation with the way of coordination to the nodes. For instance, the crystal structure obtained from the octahedral Cu^{II} associated with the ligand 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (L_4) presents a distorted diamondoid motif [48]. The adamantane cages are elongated in one direction as shown on Fig. 30, as the four molecules coordinate the copper center in equatorial positions.

Some other diamondoid metal-organic frameworks based on Ag^I as well as interpenetration structures are presented by Ciani and co-workers [49].

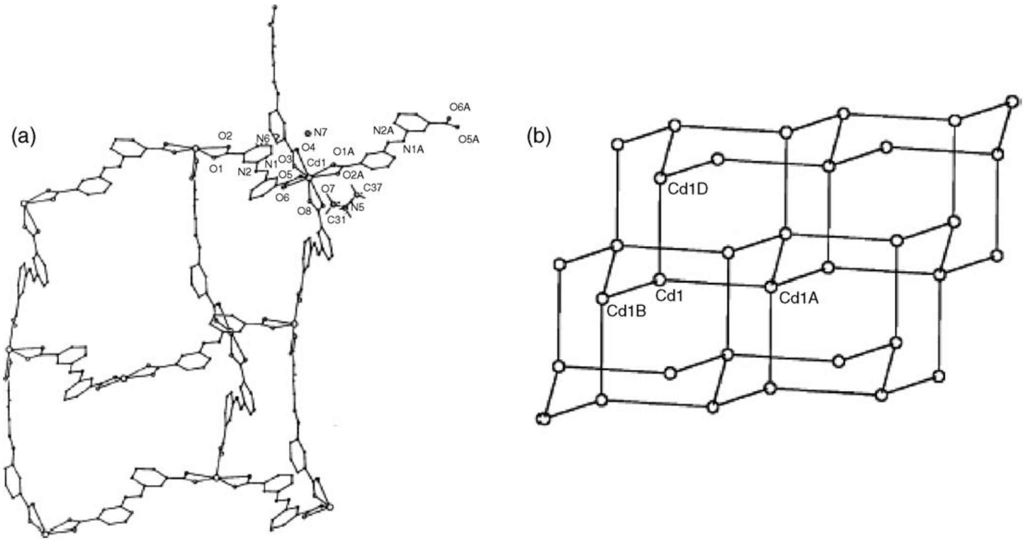


Fig. 28. (a) Adamantine unit in $\{[Cd(3,3'\text{-azdb})_2](H_2NMe_2)(NH_4)\}_n$ and (b) schematic representation of the diamondoid network in $\{[Cd(3,3'\text{-azdb})_2](H_2NMe_2)(NH_4)\}_n$ (3,3′-azdb = 3,3′-azodibenzoate). Reprinted with permission from Ref. [46]. © 2001 The Royal Society of Chemistry.

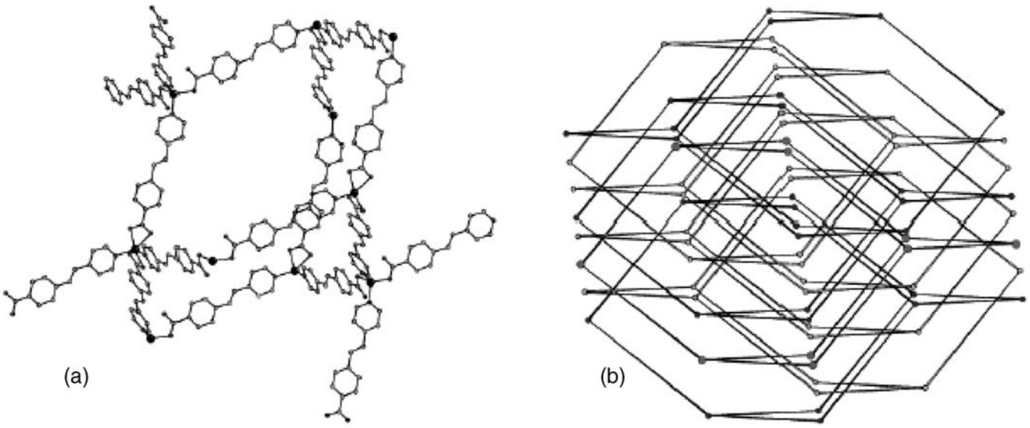


Fig. 29. $\{[Zn(L_3)_2]\}_n$: (a) the diamondoid structure and (b) schematic eight-fold interpenetration (L_3 = 4-[2-(4-pyridyl)ethenyl]benzoate). Reprinted with permission from Ref. [47]. © 2000 The Royal Society of Chemistry.

2.5.2. Octahedral net

Octahedral motifs are based on the extension of the framework in the three directions from the octahedral nodes. It is sterically very difficult to coordinate six ligand molecules around one metal center and generally the apical positions of the octahedral metal ions are occupied by water molecules, other solvent molecules or counter anions, and the resulting network is of low dimensionality. Indeed the apical positions are less often coordinated bond sites (Jahn–Teller distortion).

One of the strategies is to use two different molecules in order to build the edge of the cubical unit. SiF_6^{2-} anions, for instance, can link the metal atoms more easily than water molecules. These anions act thus as linkers between square grid layers made with the metal ions and the ligand molecules as seen in the former chapter. Moreover, the resulting three-dimensional framework is more robust as there is no uncoordinated counter ion in the structure.

The compound $\{[Cu(SiF_6)(4,4'\text{-bpy})_2]\cdot 8H_2O\}_n$ shows this organisation [50]. This compound was obtained by slow diffusion of the ligand solution (in ethylene glycol) into an aqueous ethylene glycol solution containing a mixture of $Cu(BF_4)_2\cdot 6H_2O$ and $(NH_4)_2SiF_6$. The Cu^{II} center is coordinated to four ligand molecules in the equatorial positions leading to a square grid layer. The layers are stacked together thanks to the bridging bidentate SiF_6^{2-} anions, F atoms occupying the apical sites of the Cu^{II} ions (Fig. 31a). There is no possible interpenetration in this case; channels are formed and filled with uncoordinated water molecules (Fig. 31b). This framework is very robust and remains organised even after removal of the water molecules under special conditions (373 K, reduced pressure).

The construction of octahedral motifs is also possible if the nodes are made from binuclear subunits. For example, in the compound $\{[Co(\text{terephthalate})(4,4'\text{-bpy})]\}_n$ [51] one layer is formed with terephthalate dianions capping the cobalt binuclear unit as shown on Fig. 32a and b (the carboxylate groups are coordinated to the cobalt ions in the equatorial sites). The bipyridine molecules are linked to the cobalt anions through the apical positions for the expansion of the structure in the third direction (Fig. 32c). This system is two-fold interpenetrated.

Another approach to build such three-dimensional octahedral coordination polymers is to introduce metal clusters as connecting nodes. For instance, Yaghi and co-workers present of lot of cuboidal frameworks of the type $\{[Zn_4O(L_5)_3]\}_n$ in which the ligand molecules are dicarboxylate anions [52,53]. The nodes are tetranuclear supertetrahedral cluster motifs Zn_4O. These oxide centred clusters appear by combination of metal

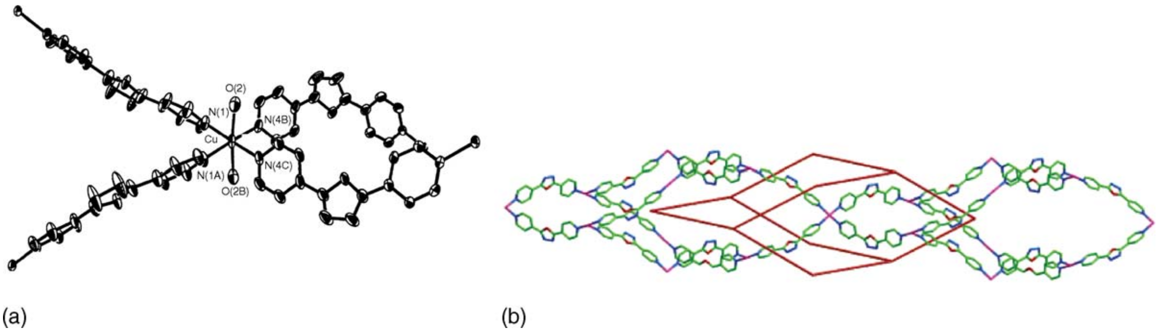


Fig. 30. (a) Coordination geometry around the Cu^{II} center and (b) the distorted adamantine cages in $\{[Cu(L_4)_2(H_2O)_2](ClO_4)(OH)(H_2O)_{2.5}]\}_n$ (L_4 = 2.5-bis(4-pyridyl)-1,3,4-oxadiazole). Reprinted with permission from Ref. [48]. © 2002 American Chemical Society.

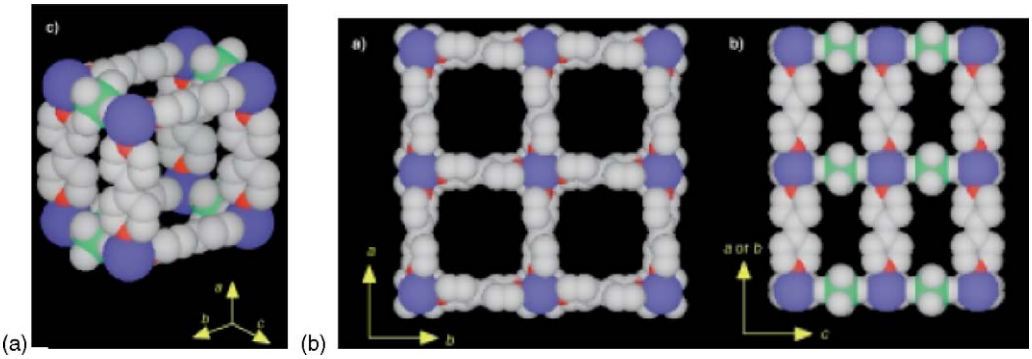


Fig. 31. (a) Cubical unit in $\{[Cu(SiF_6)(4,4'\text{-bpy})_2]\cdot 8H_2O\}_n$ and (b) view of the cavities in $\{[Cu(SiF_6)(4,4'\text{-bpy})_2]\cdot 8H_2O\}_n$ (water molecules omitted for clarity) (Cu ions in blue, Si atom in green and nitrogen atoms in red). Reprinted with permission from Ref. [50]. © 2000 Wiley–VCH Verlag. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

cations with carboxylic acids under appropriate conditions. This synthetic path was successfully extended to dicarboxylic acids. In the compound $\{[Zn_4O(bdc)_3](dmf)_8(C_6H_5Cl)\}_n$ the core of the cluster consists of one oxygen atom bonded to four Zn atoms. Each edge of the Zn_4O tetrahedron is then capped by $–CO_2$ groups of a bridging ligand molecule (1,4-benzenedicarboxylate: bdc) (Fig. 33). This core represents a secondary building block unit (SBU) interconnected by the ligands leading to the octahedral three-dimensional network (Fig. 34). Here as well, the framework maintains its morphology and crystallinity after heating to 300 °C for 1 day and thus desolvatation of the crystal has occurred.

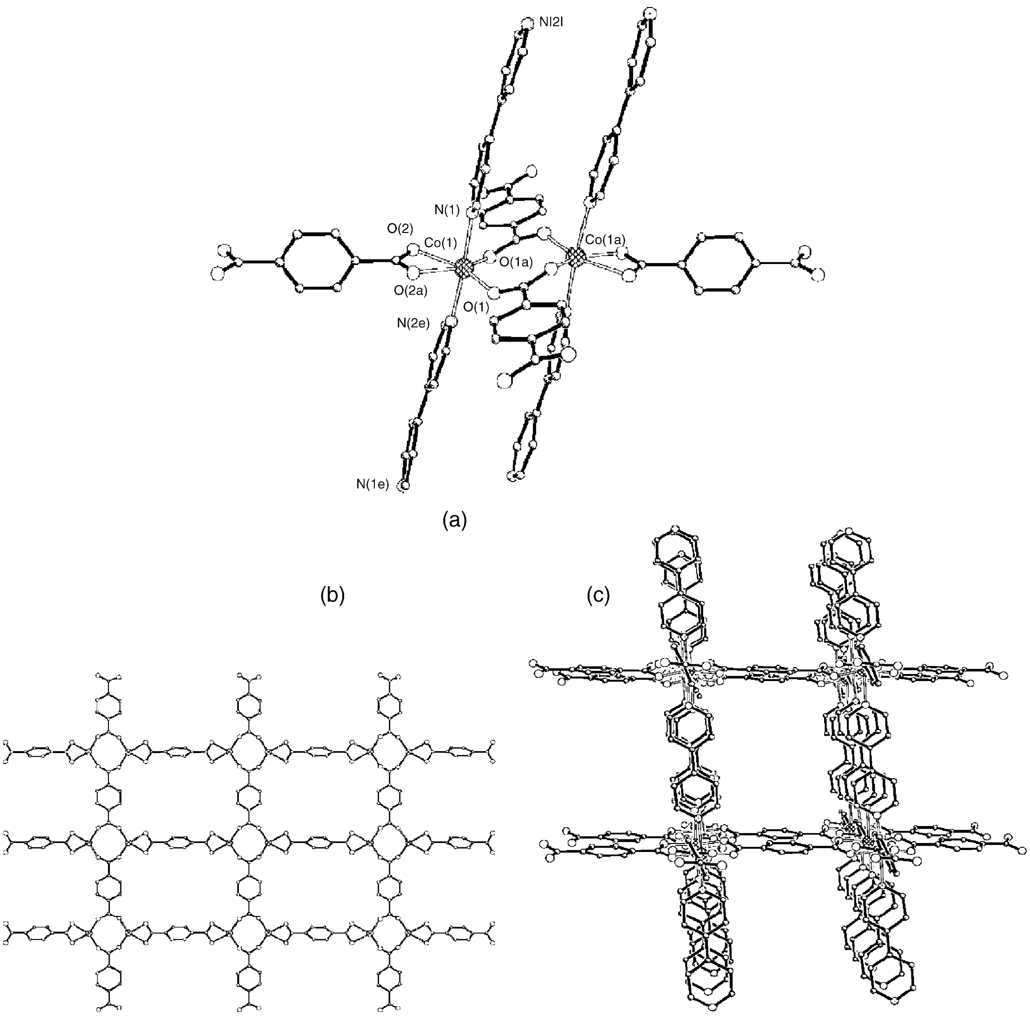


Fig. 32. Coordination polymers $\{[Co(terephthalate)(4,4'\text{-bpy})]\}_n$: (a) coordination environment of the cobalt binuclear unit; (b) Co(terephthalate) sheet and (c) perceptive view of the three-dimensional motif. Reprinted with permission from Ref. [51]. © 2000 The Royal Society of Chemistry.

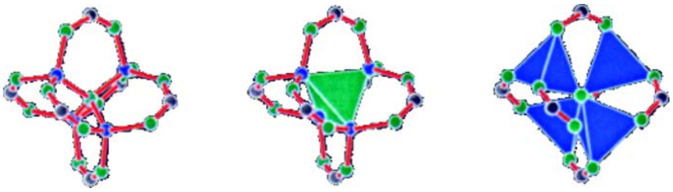


Fig. 33. Secondary building block unit (SBU) based on Zn_4O clusters and carboxylic functions in the cuboidal frameworks of the type $\{[Zn_4O(L_5)_3]\}_n$ of Yaghi and co-workers (L_5 = dicarboxylic acids). Reprinted with permission from Ref. [52]. © 1999 Macmillan Magazine Ltd.

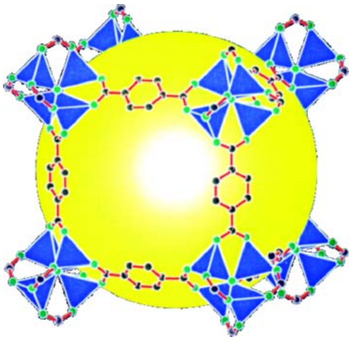


Fig. 34. Cubical unit in $\{[Zn_4O(bdc)_3](dmf)_8(C_6H_5Cl)\}_n$ the corners are the Zn_4O clusters and the edges the ligand molecules (bdc = 1,4-benzenedicarboxylate). The yellow sphere represents the internal volume; the available space in the crystal is 80% of the crystal volume. Reprinted with permission from Ref. [53]. © 2002 Science. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

2.5.3. Other 3D-motifs

An important number of other three-dimensional motifs have been observed: NbO-, $ThSi_2$-, PtS-, $SrSi_2$- and $CdSO_4$-like motifs or some intriguing and unique architectures with amazing names like ribbon-candy-like, chicken-wire-like, wave-like, accordion-like cages or other pipe-like architectures. All of these coordination polymers show a high stability; they present more or less large cavities filled with non-coordinating solvent molecules and/or with other similar networks by interpenetration.

3. Polymorphism and other isomerism

Crystallization and crystallization product studies have allowed the description of various solid state forms achieved from the same and/or different building blocks. The solids can be classified towards their composition and structure: they are defined by the repeating molecular patterns and the long-range order. This is true for the supramolecular chemistry field from pharmaceutical solids to coordination polymers ones. Some definitions for polymorphism and supramolecular isomerism were proposed in the literature for assemblies governed by molecular recognition [3,10,54–56]. The classification is not always well-defined and the following definition will be used in this paper.

If the composition of several supramolecular networks is the same, the different structures are supramolecular isomers (by comparison to molecular isomerism). Different subsets of supramolecular isomerism can be found. If differences in the nature and stoichiometry of included molecules in the networks (obtained from the same ligand, metal ion and counter anion) contribute to the formation of several metal-organic frameworks, the term pseudo-polymorphism or solvate is used.

Supramolecular isomerism is the ability of a substance to exist in more than one type of network superstructure for the same molecular building blocks. Networks are generated by different supramolecular synthons or molecular assemblies. The metal moiety and the exofunctional organic ligands remain the same but combine to give a different superstructure. There exist a lot of subsets to supramolecular isomerism.

Conformational supramolecular isomerism occurs when flexible molecular components are used. The change of ligand conformation can lead to similar motifs in which the conformation of the ligand is different from one structure to the other. For instance, Hanton and co-workers report two $[Cd(L_6)(NO_3)_2]$ (L_6 = 1,4-bis(2-pyridylmethylsulfanylmethyl)benzene) compounds showing one-dimensional chain motifs [57]. They differ in the conformation of the ligand (Fig. 35), the inclusion solvent molecules not being the same in both cases. The coordination sphere of the metal ion remains the same in the two networks.

Structural supramolecular isomers are different long-ranged organisations of the same synthons. For instance, $\{[Cu_2(\mu_2\text{-}(p\text{-benzoquinone}))(\mu_2\text{-Oac})_2]\}_n$ can form three different phases [58], the coordination of the ligands around Cu^{II} remaining the same but these synthons interacting differently (Fig. 36).

Structural isomerism is the most widely found isomerism in which the coordination sphere of the metal cation differs between the two isomers [59–63]. Two compounds of composition $\{[Co(1\text{-methyl-}1'\text{-}(3\text{-pyridyl})\text{-}2\text{-}(4\text{-pyridyl})\text{ethene})_2(NCS)_2]\}_n$ can grow concomitantly or not during the slow diffusion of two solutions of each reagent, depending on the used solvents [63]. The motif of both coordination polymers is different: one-dimensional double chain in one case and two-dimensional sheet in the other (Fig. 37). Similarly, a zero-dimensional ring-structure was obtained in parallel to a one-dimensional helical motif when $AgClO_4$ was reacted with bis(isonicontinic) glycole, both compounds crystallizing concomitantly during a diffusion experiment [35,64].

Polymorphism is the existence of the same chemical substance in more than one crystalline modification for molecular crystals. Polymorphism is scarce in the field of coordination chemistry [65] and is regarded as a subset of supramolecular isomerism: the same molecular components generate different supramolecular synthons, in other words, materials with the same chemical composition differ in the lattice structures and/or molecular conformation.

Pseudo-polymorphism is a term that refers to crystalline forms with solvent molecules as an integral part of the structure (isolated lattice sites, lattice channels or metal-ion coordinated solvates) [66–70]. The pseudo-polymorphs are obtained in crystalline forms that differ in nature or stoichiometry of included solvent molecules. The term pseudo-polymorph is

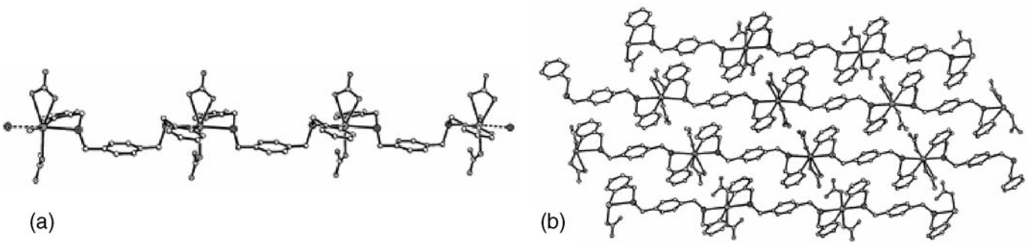


Fig. 35. One-dimensional motif in (a) $\{[Cd(L_6)(NO_3)_2]\cdot CH_2Cl_2\}_n$ and (b) $\{[Cd(L_6)(NO_3)_2]\cdot 4/3CH_3CN\}_n$ (L_6 = 1,4-bis(2-pyridylmethylsulfanylmethyl)benzene). Reprinted with permission from Ref. [57]. © 2005 American Chemical Society.

Fig. 36. The schematic representation of the three structural supramolecular isomers of $\{[Cu_2(\mu_2\text{-}(p\text{-benzoquinone}))(\mu_2\text{-Oac})_2]\}_n$ (each synthon is represented by the "rectangular" form). Reprinted with permission from Ref. [58]. © 2004 Wiley–VCH Verlag.

commonly used by researchers but is ambiguous and causes controversy in literature [71–73]. The term *solvate* is thus more convenient to describe these different solvent containing crystalline forms. Zaworotko and co-workers present solvates of $[Zn(nicotinate)_2]$ obtained under different conditions (solvent and crystallization techniques) [74]. They differ in the included solvent molecules: methanol/water or naphthalene or nitrobenzene. The motifs and dimensionalities of these compounds are very different and influenced by the reaction conditions. Fromm et al. have reported solvates for one-dimensional copper coordination polymers obtained from CuCl and ethanediyl bis(isonicotinate) (=L_1), once including THF as solvent to yield red $\{[Cu(L_1)(Cl)]\cdot 0.5THF\}$ and once without solvent yielding the yellow $[Cu(L_1)Cl]$ [19,35]. The same ligand and $AgNO_3$ give three different solvates $\{[Ag(NO_3)(L_1)]\cdot(H_2O)_n\}$ from similar reaction media, with dramatically different structures, depending if zero, one or two water molecules co-crystallize [35,75].

During crystallization the traditional thermodynamic versus kinetic game plays an important role. The different solid state forms can appear under different conditions [59,61,63,66–68,74,76] or as a mixture in the same batch [60,63,70,77]. In some examples, isomers are found in the same crystal with two concomitant motifs [78].

Such phenomena could be regarded as drawback and one more difficulty in the prediction of molecular recognition, but they should be seen as a better understanding of the building blocks, and the self-assembly process. They allow us to know the finite number of possible structures. These phenomena appear

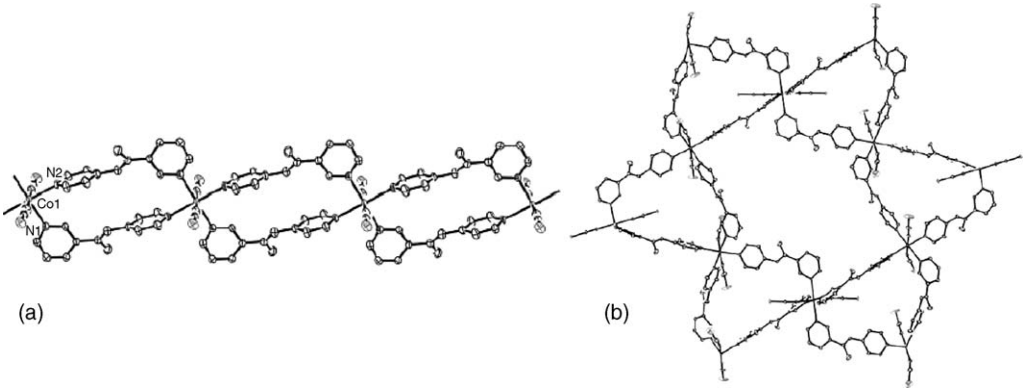


Fig. 37. The two structural supramolecular isomers of $\{[Co(1\text{-methyl-}1'\text{-}(3\text{-pyridyl})\text{-}2\text{-}(4\text{-pyridyl})ethene)_2(NCS)_2]\}_n$: (a) double chain and (b) sheet. Reprinted with permission from Ref. [63]. © 2004 Wiley–VCH Verlag.

more frequently the more flexible systems and the more functionalized groups are involved.

4. Possible applications

One of the interests in building coordination polymers is the creation of new tuneable functional materials. In this part of the review, we will present examples of how metal-organic frameworks are promising as materials for applications in gas storage, anion exchange (due to the porosity and zeolitic-like behaviour), catalysis, conductivity, luminescence, chirality, magnetism, spin transition behaviour, NLO or deposition of thin films.

4.1. Porous materials

Controlled porosity in materials is a widely studied topic in chemistry, as open frameworks with micro- or nanometre-sized cavities can be used in gas and liquid separation, gas storage, sensors, molecular recognition, anions/cations exchange, heterogeneous catalysis, . . . [79]. Indeed porous materials allow the reversible passage of host molecules through the guest materials via the surface holes. Some inorganic materials are commonly used such as zeolites and activated carbons. Zeolites are micro porous crystalline solids containing generally silicium and aluminium oxides. They are extensively used in a lot of industrial processes. Activated carbons are twisted networks of defective hexagonal carbon layers, cross linked by aliphatic bridging groups showing a high open porosity and a high specific surface area. The advantage of introducing organic molecules in such frameworks is the control of the material design: architecture choice, functionality of the pores and increasing selectivity.

The coordination polymers have to be highly crystalline and porous, but it is well-known that free space is against nature in crystals. When cavities appear in these frameworks, they are filled either by interpenetration or by counter ions, solvents molecules or additional co-crystallizing organic molecules. These latter molecules can be regarded as templates determining the pore shapes and sizes. As the metal-organic frameworks bonds are non-covalent bonds, the removal of the template molecules can lead to structure collapsing. That is why scientists search for metal-organic frameworks with permanent crystalline structures even after the removal or exchange of the guest molecules.

Porous coordination materials can be divided in three categories:

- the *first generation* porous materials contain cavities and/or channels but these structures lose their crystallinity after removal of the guest molecules (collapsing) and are not useful for the required applications (see further);
- the *second generation* metal-organic frameworks remain crystalline and stable as they are totally desolvated and they have a zeolitic behaviour;
- the *third generation* frameworks are dynamic and flexible ones which respond to external stimuli (like light, electric field, magnetic field and guest molecules) in changing their structures.

The transformation during the removal of the guest molecules is regarded as a “crystal-to-amorphous transformation” in the first generation metal-organic frameworks, whereas the transformations in the two other cases are named “crystal-to-crystal” ones [80].

Gas storage is one of the possible applications for these materials. As seen previously, the compound $\{[Zn_4O(dcx)_3]\}_n$ (dcx = dicarboxylate) [52] shows large channels. The channel sizes can be tuned by the use of appropriate ligand molecules. In the compound $\{[Zn_4O(bdc)_3](dmf)_8(C_6H_5Cl)\}_n$ obtained with 1,4-benzenedicarboxylate (bdc) molecules as ligands, the dmf and chlorobenzene molecules can be removed. The total crystal desolvation and desolvated crystal stability was proven, and the sorption behaviour was studied with nitrogen, argon and organic vapors of molecules such as CH_2Cl_2, $CHCl_3$, CCl_4, C_6H_6 and C_6H_{12}. Yaghi and co-workers report also other coordination polymers based on bis- and tris-bidentate carboxylate linkers copolymerized with Zn^{II}. In these compounds the nodes are rigid metal carboxylate clusters, which allow the stability of the porous materials. The sorption processes are well studied affording efficient and robust materials for gas storage or liquid separation [53,81–83].

The compound $\{[Cu(SiF_6)(4,4'\text{-bpy})_2]\cdot 8H_2O\}_n$ described below (Fig. 31) presents similarly a robust three-dimensional network. The methane absorption experiments show high adsorption ability and good morphology/crystallinity retention [50].

A beautiful example given in a review on sulfonates by Cote and Shimizu [84] deals with a third generation framework. The silver coordination network can reversibly lose and take up selectively acetonitrile vapors, changing its symmetry (Fig. 38) from triclinic (solvated form: $\{[Ag(L_7)(CH_3CN)_{0.5}]\}_n$) to tetragonal (desolvated form: $\{[Ag(L_7)]\}_n$) and vice versa (L_7 = 3-pyridinesulfonic acid).

Kitagawa and co-workers report also a third generation pillared-layer coordination polymer able of solvent removal and specific guest molecule re-inclusion [85]. The structure of this compound is made by two-dimensional layers $Cu_2(pzdc)_2$ (pzdc = pyrazine-2,3-dicarboxylate) connected with additional dpyg molecules (dpyg = 1,2-dipyridylglycol) in order to build a porous three-dimensional coordination polymer, the free space being initially filled with water molecules (Fig. 39). The material is able to lose the co-crystallized water molecules (at 60 °C) and an X-ray powder diffraction (XRPD) study shows two guest free phases: the anhydrous one I (same structure without the water molecules) and the apohost II (in which the inter-layer distances are smaller). Adsorption isotherm measurements prove that phase II can selectively adsorb CH_3OH and H_2O but not CCl_4, and that the final product (including the guest molecules) has the initial structure. In the absence of guest molecules, the layers get also closer to each other, the material adjusting to avoid the free space.

The Kitagawa group works on materials capable of structural changes in response to the guest molecules: the cavities or channels adapt their shapes in order to fit around the guest molecules [86,87]. A schematic representation is shown on Fig. 40. These materials do not lose their robustness and

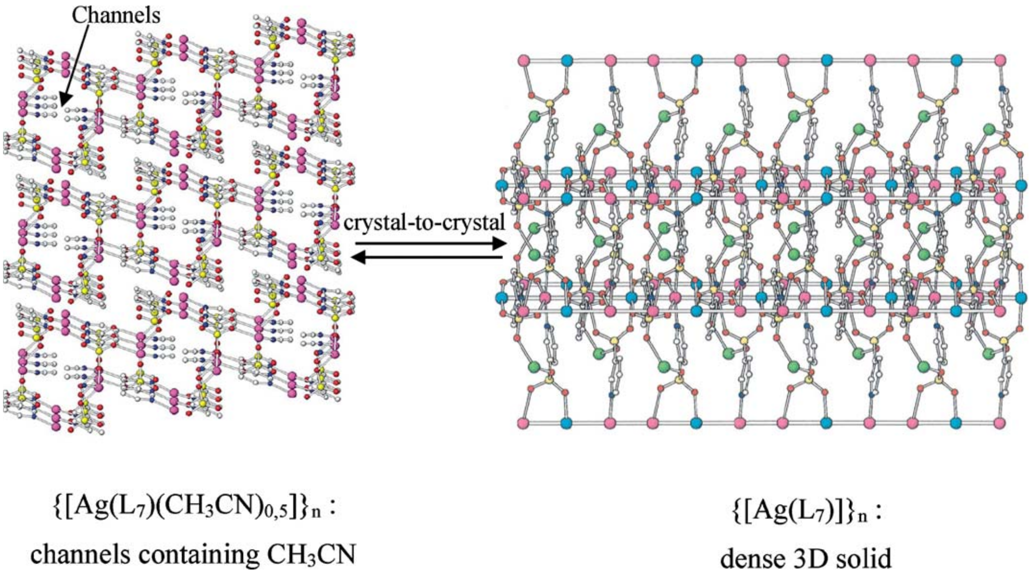


Fig. 38. Triclinic to tetragonal shift in the solid state between $\{[Ag(L_7)(CH_3CN)_{0.5}]\}_n$ and $\{[Ag(L_7)]\}_n$ (L_7 = 3-pyridinesulfonic acid). Reprinted with permission from Ref. [84]. © 2003 Elsevier.

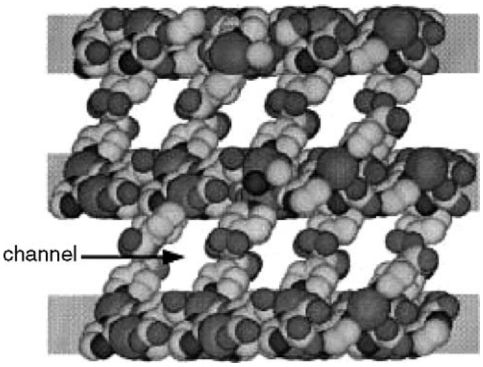


Fig. 39. 3D view of the layers, pillars and channels in $\{[Cu_2(pzdc)_2(dpyg)]8H_2O\}_n$ (water molecules omitted for clarity; pzdc = pyrazine-2,3-dicarboxylate; dpyg = 1,2-dipyridylglycol). Reprinted with permission from Ref. [85]. © 2002 Wiley–VCH Verlag.

are potential candidates for target molecule recognition or separation.

Another type of third generation metal-organic framework is presented by Wright and co-workers with compounds made from zinc^{II} benzene-dicarboxylates (bdc) [88]. A series of [Zn(bdc)] coordination polymers is reported with solid state transformations by removal or replacement of strongly hydrogen-bonding molecules: DMF, methanol, ethanol or water as resumed on Fig. 41. All of these compounds have characteristic structures implying a lot of structural changes during the transformations.

Soldatov and Ripmeester report species able of gas inclusion [89,90]. The $\{[Cu(L_8)_2]\}_n$ ($L_8 = CF_3COCHCOC(OMe)Me_2$) complex exists in two forms: the α-form containing no pores

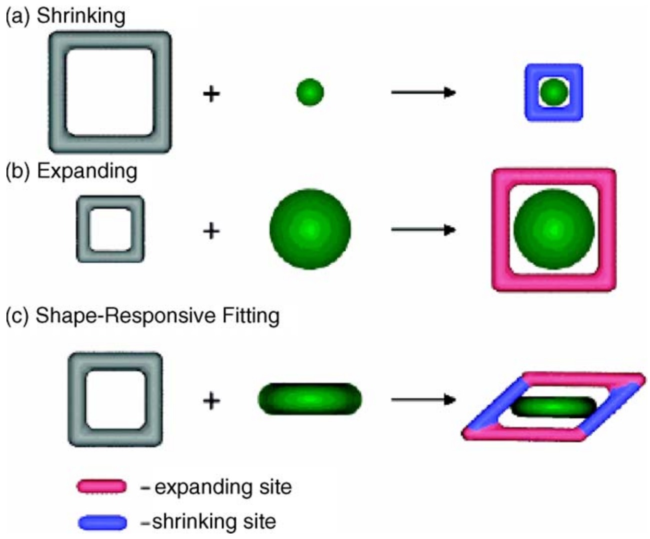


Fig. 40. Schematic representation of the responsible coordination polymer networks. Reprinted with permission from Ref. [86]. © 2004 American Chemical Society.

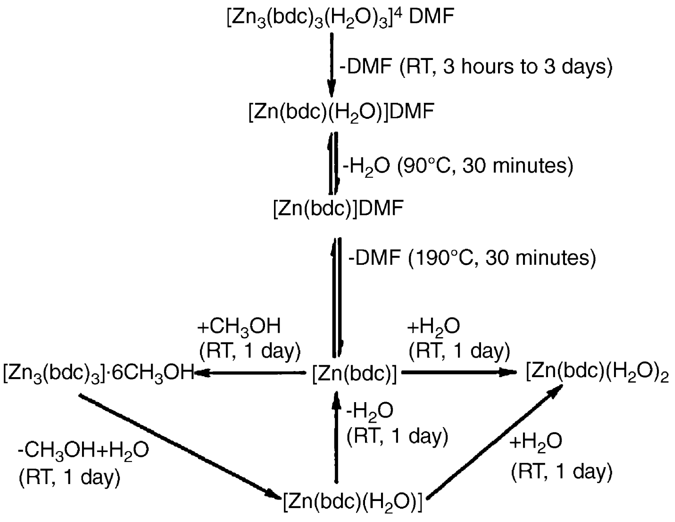


Fig. 41. Desolvation and re-solvation reaction summary for the zinc^{II} benzene-dicarboxylates. Reprinted with permission from Ref. [88]. © 2001 Wiley–VCH Verlag.

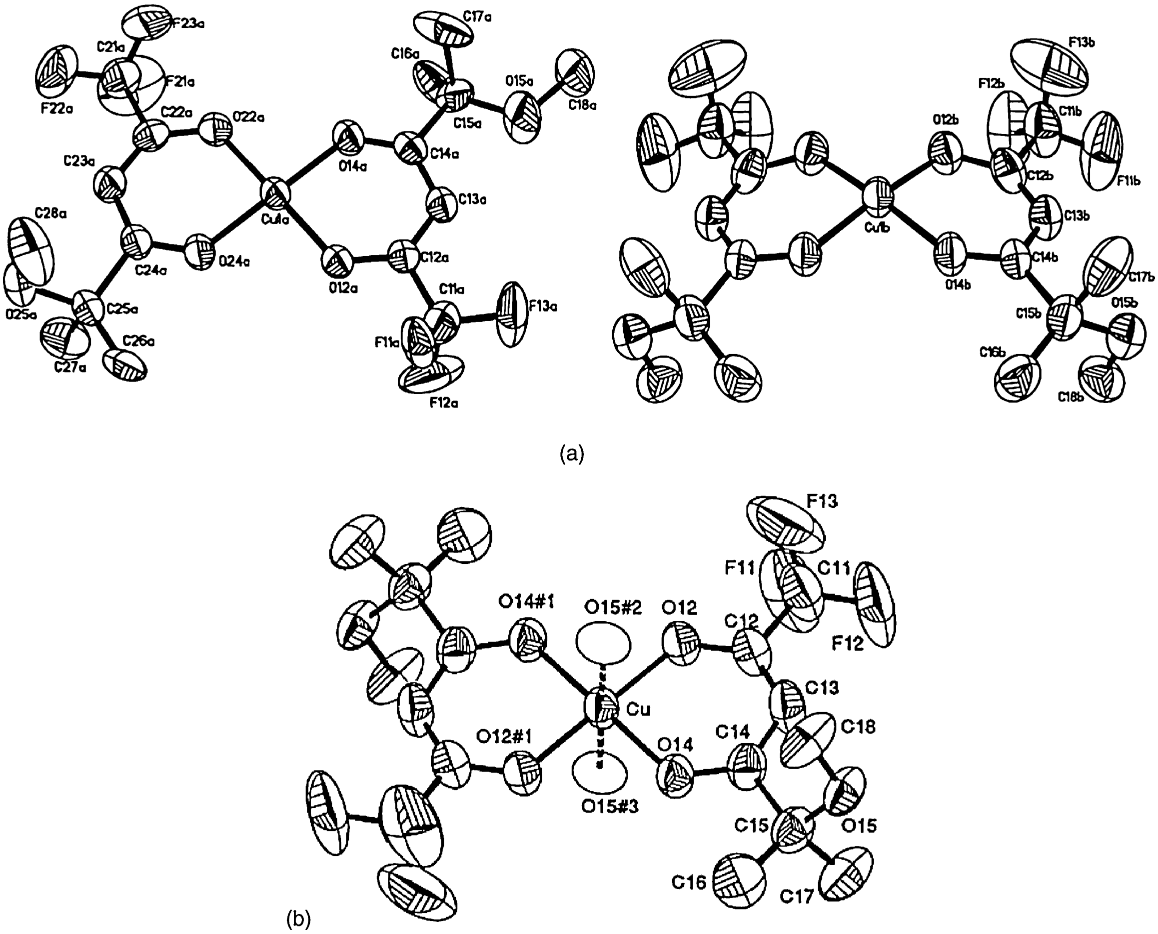


Fig. 42. (a) α-Form (there is two crystallographically independent complex units) and (b) β-form of $\{[Cu(CF_3COCHCOC(OMe)Me_2)_2]\}_n$. Reprinted with permission from Ref. [89]. © 1999 American Chemical Society.

in the structure and the β-one having channels of about 6 Å in diameter (Fig. 42).

Exposed to alcohol vapors, the α-form can transform itself simultaneously with the inclusion of the alcoholic guest molecules, although this form does not have any pores. Two phenomena are observed: in the case of methanol and ethanol exposures, new compounds appear in which the guest molecules coordinate the unsaturated copper atoms leading, respectively, to the compounds $[Cu(L_8)_2(MeOH)_2]$ and $\{[Cu(L_8)_2(MeOH)]_2[Cu(L_8)_2]\}_n$ (Fig. 43). There are no free voids in these structures.

Under longer alcohol gas exposure, the α-form transforms into the cavities containing β-form with inclusion of the alcohol molecules in the free space. The two phenomena are described as chemical or physical inclusions depending on the role of the hydrophobic part in the alcohol molecules which are capable of more or less strong van der Waals interactions with the wall

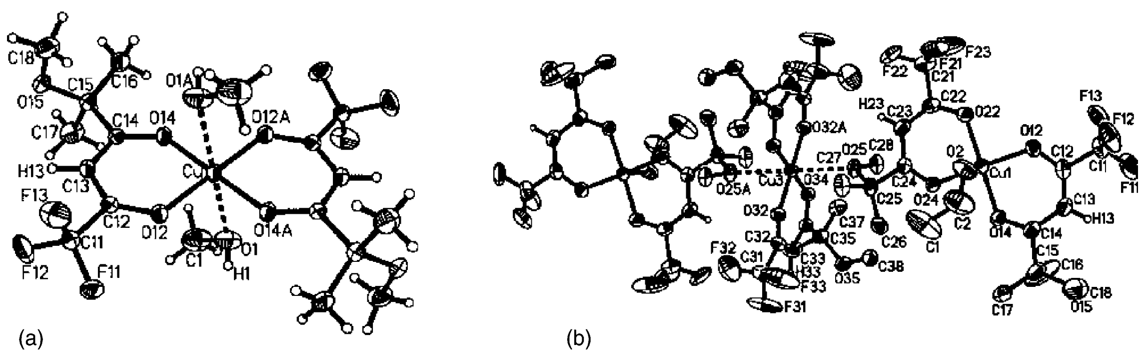


Fig. 43. (a) The molecule $[Cu(L_8)_2(MeOH)_2]$, the overall structure is a two-dimensional structure achieved trough hydrogen bonds and (b) the trinuclear unit of one-dimensional coordination polymer $\{[Cu(L_8)_2(MeOH)]_2[Cu(L_8)_2]\}_n$ ($L_8 = CF_3COCHCOC(OMe)Me_2$). Reprinted with permission from Ref. [90]. © 2000 American Chemical Society.

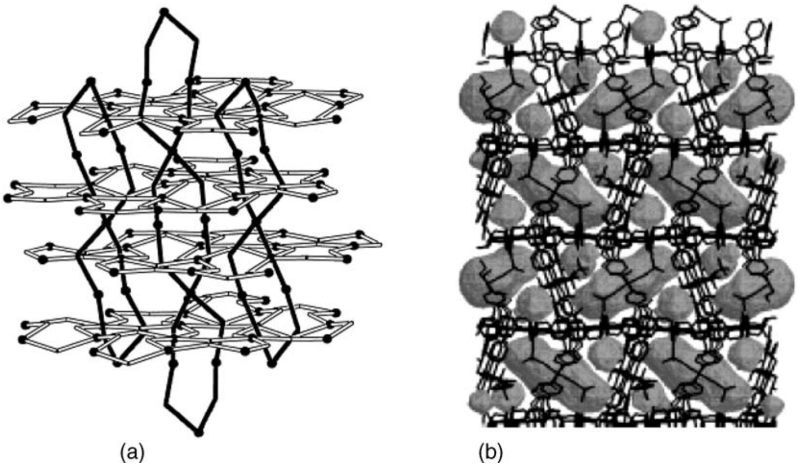


Fig. 44. $\{[Cu_5(bpp)_8(SO_4)_4(EtOH)(H_2O)_5](SO_4)\cdot EtOH\cdot 25,5H_2O\}_n$: (a) Schematic view of the entanglement of the 1D motif (in black) and the 2D motif (in white) and (b) distribution of the empty cavities (their limiting surface are show in grey). Reprinted with permission from Ref. [91]. © 2000 Wiley–VCH Verlag.

cavities. The material can catalytically switch between dense or open forms. The same observation is made in wetting the α-form in different saturated solutions of guest molecules. Depending on the guest molecules, the α-to-β transformations is observed, or new $[Cu(L_8)_2Guest2]$ compounds appear.

Among the few examples of dynamic systems the following example is also interesting. Ciani and co-workers synthesized a three-dimensional coordination polymer via the self-assembly of Cu^{II} sulfate salt with 1,3-bis(4-pyridyl)propane (bpp) ligand molecules: $\{[Cu_5(bpp)_8(SO_4)_4(EtOH)(H_2O)_5](SO_4)\cdot EtOH\cdot 25,5H_2O\}_n$ [91]. The three-dimensional structure is achieved by the entanglement of a one-dimensional structural motif within a two-dimensional one (Fig. 44a).

About 1/4 of the cell volume is constituted of large voids containing the solvated molecules of ethanol and water (Fig. 44b). The loss of these solvent molecules was followed by thermogravimetric analysis (TGA). The desolvation is accompanied with a loss of order, but in presence of water vapors the crystallinity reappears. The process is also reversible. The rehydration was followed by observation of the crystal surfaces (atomic force microscopy, AFM).

Another type of exchange is reported by Navarro and co-workers [92]. The compound $\{[Cu(pymo\text{-}N1,N3)_2]\cdot NH_4ClO_4 = \mathbf{1}\cdot NH_4ClO_4$ (Hpymo = 2-hydroxypyrimidine) shows an open framework. The free voids are organised in order to form a diamondoid network containing water, ammonia and perchlorate molecules (Fig. 45).

By heating, the crystals can lose NH_3 molecules leading to the crystalline $\mathbf{1}\cdot HClO_4$ and are recovered by exposure to gaseous NH_3. A salt inclusion is possible too. Indeed, if the isolated compound **1** is exposed to $AClO_4$ aqueous solutions ($A = NH_4^+$, Li^+, Na^+, K^+ and Rb^+), $\mathbf{1}\cdot AClO_4$ is formed undergoing phase changes. This compound belongs to the third generation open metal-organic frameworks and is a rare example of *salt sorption*.

Finally, *exchange of anions* can be performed as well using such open metal-organic frameworks. Zeolites are anionic frameworks and can only be used as cations exchangers. By using cationic ions and neutral ligand molecules as it is usually done for coordination polymer networks, it is, however, possible to get cationic networks and to create anionic exchangers.

The process of anion exchange takes place at a solid–liquid interface and is a solid state transformation. In this context,

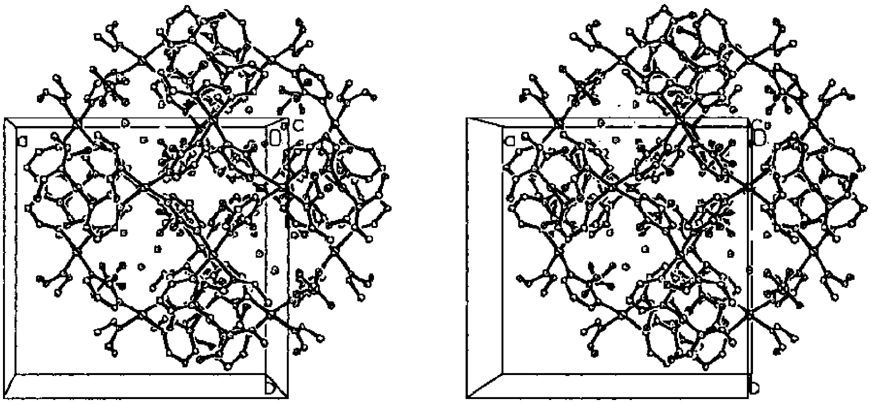


Fig. 45. Stereo-view of the three-dimensional void network in $\{[Cu(pymo\text{-}N1,N3)_2]\cdot NH_4ClO_4$ (Hpymo = 2-hydroxypyrimidine). Reprinted with permission from Ref. [92]. © 2001 American Chemical Society.

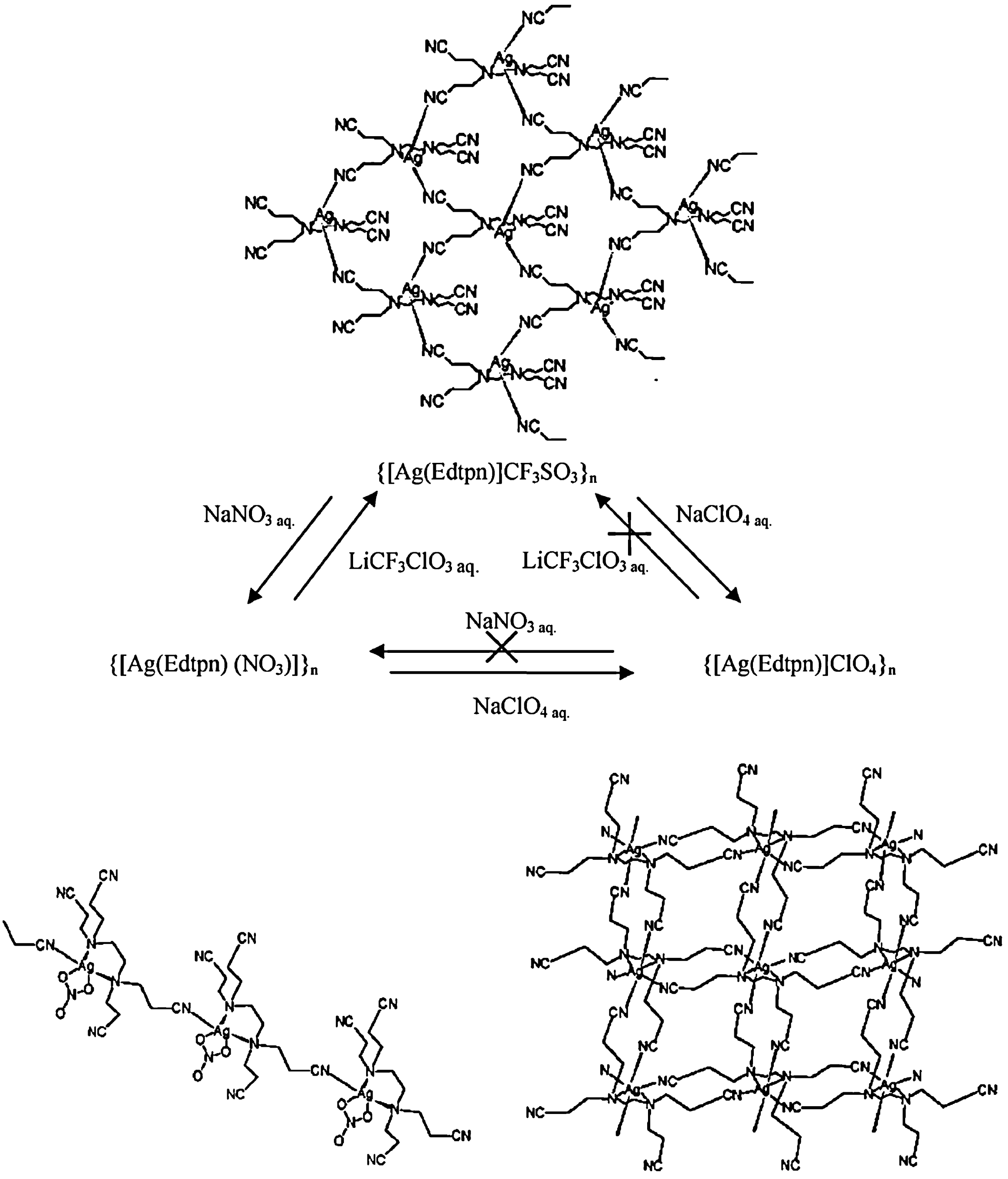


Fig. 46. Exchange of anions scheme in the coordination polymers: $\{[\mathrm{Ag(Edtpn)}]\mathrm{CF_3SO_3}\}_n$ (Edtpn = ethylenediaminetetrapropionitrile). Reprinted with permission from Ref. [93]. © 2000 American Chemical Society.

Min and Shu report coordination polymers based on ethylenediaminetetrapropionitrile ligand molecules (Edtpn) and silver salts (nitrate, perchlorate and triflate) [93]. Some anion exchanges happen during the immersion of the crystals in appropriate aqueous solutions of $NaNO_3$, $NaClO_4$ or $LiCF_3SO_3$. As shown on Fig. 46, the triflate anions can be quantitatively and reversibly exchanged with the nitrate anions. The triflate anions can also be exchanged with the perchlorate anions, and the nitrate compound can change its structure in including perchlorate anions. The authors claim that these exchanges and structural transformations occur in the solid state. They were followed by XRPD and IR measurements.

An important application of the coordination polymer networks is *catalysis*. The coordination polymers may be helpful as (1) they can be porous, (2) they can contain catalytically active transition metal centers and (3) they can be designed in order to offer metal centers and specific organic groups to the reagents. Some non-porous coordination polymers are nevertheless also known for their catalytical properties. Heterogeneous catalysis is obviously considered with the use of the coordination poly-

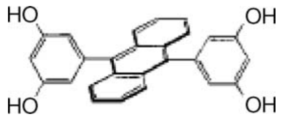
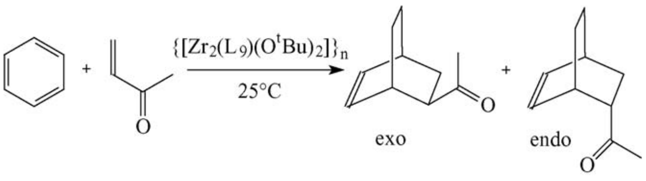


Fig. 47. Anthracenebisresorcinol (L_9). Reprinted with permission from Ref. [94]. © 2001 American Chemical Society.

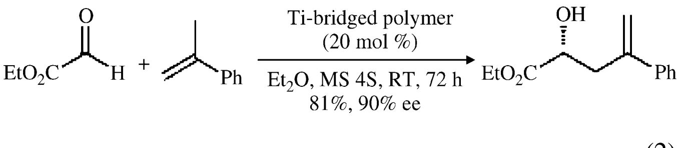
mer in crystalline form. A notable drawback in the use of these compounds for heterogeneous catalysis is their stability in the liquid phase: they should not dissolve or degrade at all during the catalytic cycle; otherwise ligand molecules and metal centers would react or interact.

Only few examples of such materials with an efficient catalytic activity can be found in the literature. Coordination polymers based on anthracenebisresorcinol (H_4L_9; Fig. 47) treated with $Al(CH_3)_3$, $Ti(O^iPr)_2Cl_2$, $Zr(O^tBu)_4$ or $La(O^iPr)_3$ are studied by Aoyama and co-workers and show catalytic activities [94–97]. For instance, the Zr host compound $\{[Zr_2(L_9)(O^tBu)_2]\}_n$, whose structure is unknown (as it is insoluble in all common organic solvents), is described as a microporous framework. It can act as a reversible guest molecule acceptor (ethylacetate, benzene, hexane, ...) and as catalyst for Diels–Alder reactions (see Eq. (1), reprinted with permission from Ref. [2]. © 2003 The Royal Society of Chemistry) with a good selectivity (endo:exo = 95:5), and there is no contamination of the catalytic solution.



(1)

Recently, several groups discovered metal-organic frameworks suitable for heterogeneous asymmetric catalysis [98]. The aim of these materials is to provide cavities walled with chiral environments for enantioselective control and with available metal ions as catalytic active centers. The groups of Sasai and Ding [99,100] generate chiral metal-organic coordination polymers thanks to the self-assembly of a chiral ligand containing two 1,1′-2,2′-binaphtol units (binol) (Fig. 48) and Al^{3+}, Ti^{2+} ions. These compounds are highly insoluble in common organic solvents. The compound $\{[Ti_2(\mu\text{-}O)_2(binol)]\}_n$ (Fig. 49) is employed as catalyst in the asymmetric carbonyl-ene reaction shown on Eq. (2) (reprinted with permission from Ref. [99]. © 2003 Wiley–VCH Verlag). The product was obtained with results comparable to those reached with the classical homogeneous catalyst.



(2)

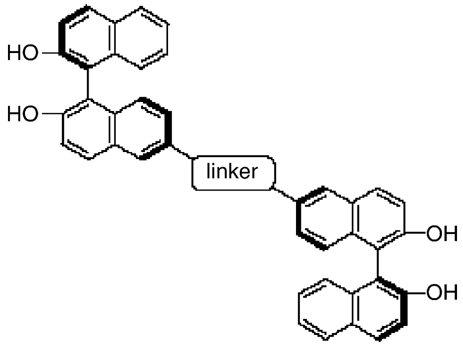


Fig. 48. Chiral ligand containing two 1,1′-2,2′-binaphtol units. Reprinted with permission from Ref. [100]. © 2004 Elsevier.

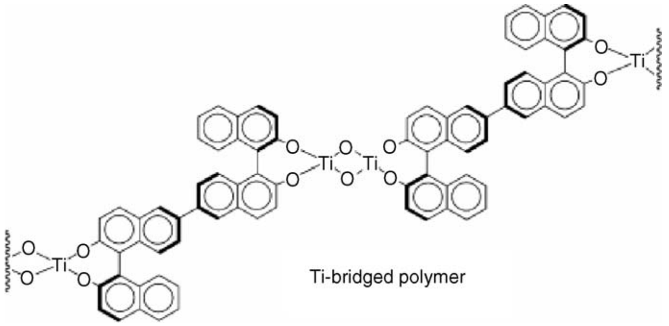


Fig. 49. Coordination mode of $\{[Ti_2(\mu\text{-}O)_2(binol)]\}_n$ obtained with the reaction of the ligand in which the linker is a single bond with $Ti(O^iPr)_4$. Reprinted with permission from Ref. [99]. © 2003 Wiley–VCH Verlag.

The non-porous coordination polymer $\{[In_2(OH)_3(bdc)_{1.5}]\}_n$ (Fig. 50) (bdc = 1,4-benzendicarboxylate) shows a catalytic activity for the hydrogenation of nitroaromatics (Eq. (3)a) and oxidation of sulfide reactions (Eq. (3)b, reprinted with permission from Ref. [2]. © 2003 The Royal Chemical Society).

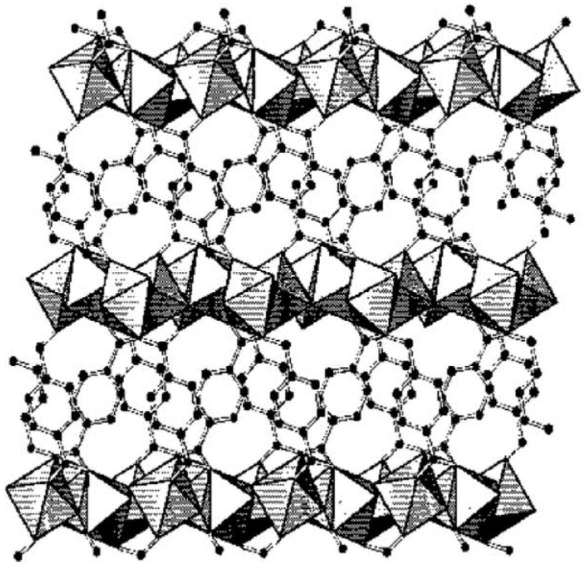


Fig. 50. The three-dimensional network of $\{[In_2(OH)_3(bdc)_{1.5}]\}_n$ is made of two-dimensional $\{[In_2(OH)_3]^{2+}\}_n$ sheets pillared with the bdc ligand molecules (bdc = 1,4-benzendicarboxylate). Reprinted with permission from Ref. [101]. © 2002 American Chemical Society.

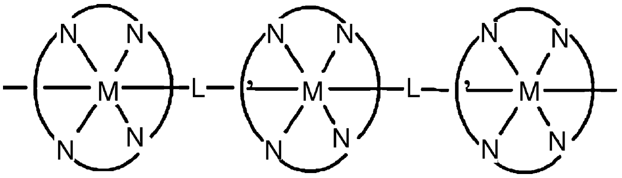
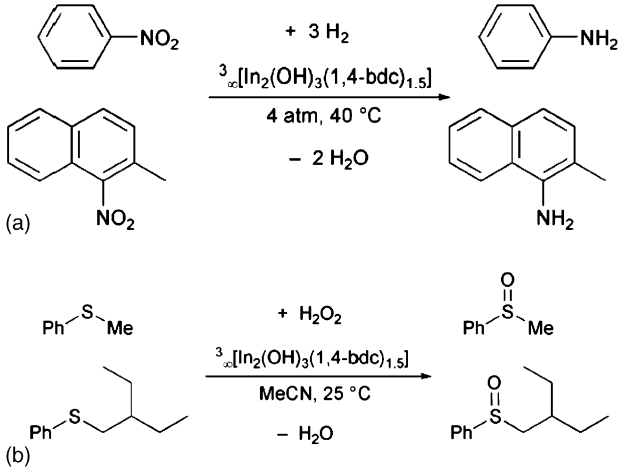


Fig. 51. $\{[ML_{10}(\mu\text{-}L_{11})]\}_n$ coordination polymers with M = Fe, Ru, Os; L_8 = octaethylporphyrinato or phthalocyaninato; L_{10} = pyrazine or 4,4′-bipyridine. Reprinted with permission from Ref. [102]. © 1988 Elsevier.

Although the catalytic mechanism is not totally understood, it must take place at the surface and involves coordinative unsaturations either with ligand dissociation or with increase in the coordination number of indium [101].



(3)

4.2. Conductivity

Conductivity may be an interesting research topic providing that short inorganic or conjugated organic bridges exist in the metal-organic framework.

Some one-dimensional coordination polymers $\{[M(L_{10})(\mu\text{-}L_{11})]\}_n$ built as shown on Fig. 51 with or without doping with iodine exhibit conductivities in a range of 1×10^{-6} to $2\times10^{-1}\,\mathrm{S\,cm^{-1}}$ [102]. (Conductivity of metals is 10^4–$10^5\,\mathrm{S\,cm^{-1}}$ and increases with decreasing temperature.) The conductivity is due to the interaction between the metal d-orbital and the π^* level of the bridging ligand L_{11}.

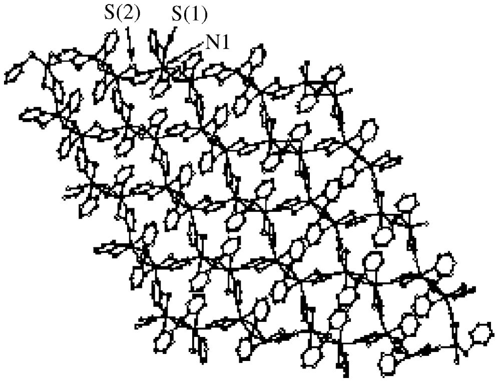


Fig. 53. View of the lamellar structure of $\{[Ni_2(\text{pyrimidine-2-thiolate})]\}_n$. Reprinted with permission from Ref. [105]. © 2001 The Royal Society of Chemistry.

In some cases coordination polymers can have semi-conductor behaviour. The three-dimensional polymer $\{[Ag(H_2btc)_2][Ag_2(Hbtc)]\}_n$ (H_3btc = benzene-1,3,5-tricarboxylate) [103] presents weak semi-conductivity (conductivity of $1.06\times10^{-6}\,\mathrm{S\,cm^{-1}}$ and increase of conductivity with temperature) due to the presence short Ag–Ag contacts as the whole structure can be regarded as parallel Ag chains connected by the H_2btc^{-} and $Hbtc^{2-}$ ligands (Fig. 52). The Ag–Ag contacts, ranging from 2.9626 to 3.2782 Å, are known for giving semi-conductivity properties to the materials.

The semi-conductivity is better for the compound $Ag_2{\cdot}CA$ (CA = cyanuric acid, $C_3H_3N_3O_3$) being an organic–inorganic hybrid material. It is composed of Ag sheets with the cyanuric acid as linkers between the sheets. The conductivity is furthermore anisotropic in this case, 5×10^{-3} parallel to the sheets, and $2\times10^{-5}\,\mathrm{S\,cm^{-1}}$ perpendicular to the sheets [104].

Semi-conductivity was also reported for the compound $\{[Ni_2(\text{pyrimidine-2-thiolate})]\}_n$ which exhibits two-dimensional motifs based on Ni_2S_2 units spaced out by the ligand molecules [105] (Fig. 53). There are therefore short distances between the metal centers of 3.774 Å. Its conductivity is found to be $5\times10^{-3}\,\mathrm{S\,cm^{-1}}$ at 28 °C and increases with temperature. The semi-conductivity provides evidence for nickel and pyridine ring interactions.

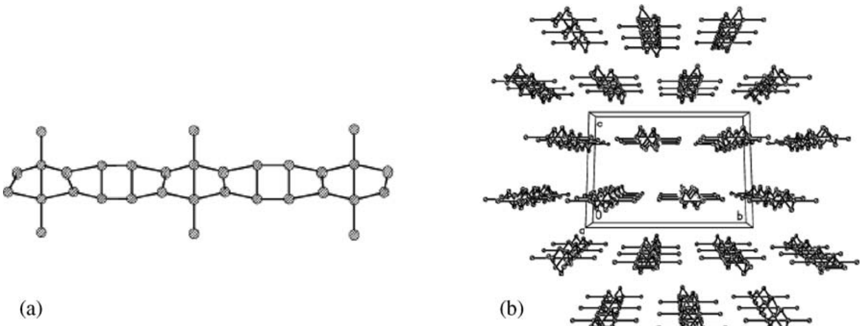


Fig. 52. The Ag chains in $\{[Ag(H_2btc)_2][Ag_2(Hbtc)]\}_n$ (organic spacers omitted for clarity) (H_3btc = benzene-1,3,5-tricarboxylate). Reprinted with permission from Ref. [103]. © 2002 The Royal Society of Chemistry.

4.3. Luminescence

Luminescent supramolecular architectures have recently attracted much interest because of their potential applications in optoelectronic devices or as fluorescent sensors and probes. Indeed inorganic–organic coordination polymers often afford more stability (thermal- and solvent-resistant) than the pure organic ligands and may affect the emission wavelength of these organic molecules.

Determination of the fluorescence is usually made in the solid state and mostly at room temperature. In some cases fluorescence measurements are also made in solution in order to prove the existence of oligomeric fragments [106,107]. Different phenomena can explain the luminescence observed in related luminescent coordination polymers, they would be discussed in the following chapter.

Emissions may be assigned in a significant number of examples to ligand-to-metal charge transfer (LMCT), if the luminescence is due to the metal–ligand complex formation [103,108–114]. The intense photoluminescence emission of these materials can be used in order to design potential candidates for emitting diode devices. The two compounds $\{[Tb(O_2CPh)_3(CH_3OH)_2(H_2O)]\}_n$ and $\{[Tb_2(O_2CPh)_6(4,4'\text{-bipyridine})]\}_n$ (Fig. 54a and b) present strong bright green emission and their emission spectra are almost identical (Fig. 54c and d). The emission is due to LMCT processes [113]. Indeed the emission bands of the ligand molecules do not appear in the spectra. Thus, the ligand transfers the excitation energy efficiently to the Tb^{III} ions, the four bands corresponding, respectively (from left to right) to the transitions $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$.

In some other cases the fluorescence intensity can be significantly enhanced in the polymeric compound in comparison to the one of the pure organic molecules without change in the emission wavelength [22,115–122]. It is only due to contribution of the organic part, the enhancement coming from the increase in the rigidity of the ligand molecules in the complexes and/or the decrease of the symmetry within the ligand molecules. Sometimes red- or blue-shift is observed due to particular interactions (π–π stacking) or to (de)protonation of the ligand. The emission of the compound $\{[Cd(\text{terephthalato})(\text{pyridine})]\}_n$ occurs at 464 nm while the terephthalato acid emits at 466 nm. But the intensity of the complex emission is 100 times larger than that of the free ligand. The emission is due to intraligand π–π* transitions [115]. The same observation is made with the compound $[Cu(PPh_3)(N,N\text{-(2-pyridyl)(4-pyridylmethyl)amine})_{1.5}]\cdot 0{,}5CHCl_3\cdot ClO_4\}_n$: the free ligand emits at 460 nm whereas the complex emits at 490 nm with an intensity 10 times larger. The weak bathochromic shift is probably due to the increase of aromatic π–π stacking in the crystalline metal-organic frameworks [118].

Silver coordination polymers display weak luminescence at room temperature [123]. They are known to be greater emitting materials at low temperature [124], with an enhancement of the emitting intensity [76] and/or a shift of the emission wavelength [124]. In the particular case of coordination polymers containing silver–silver contacts, the luminescence properties may be assigned to the short metal–metal contacts [125–127].

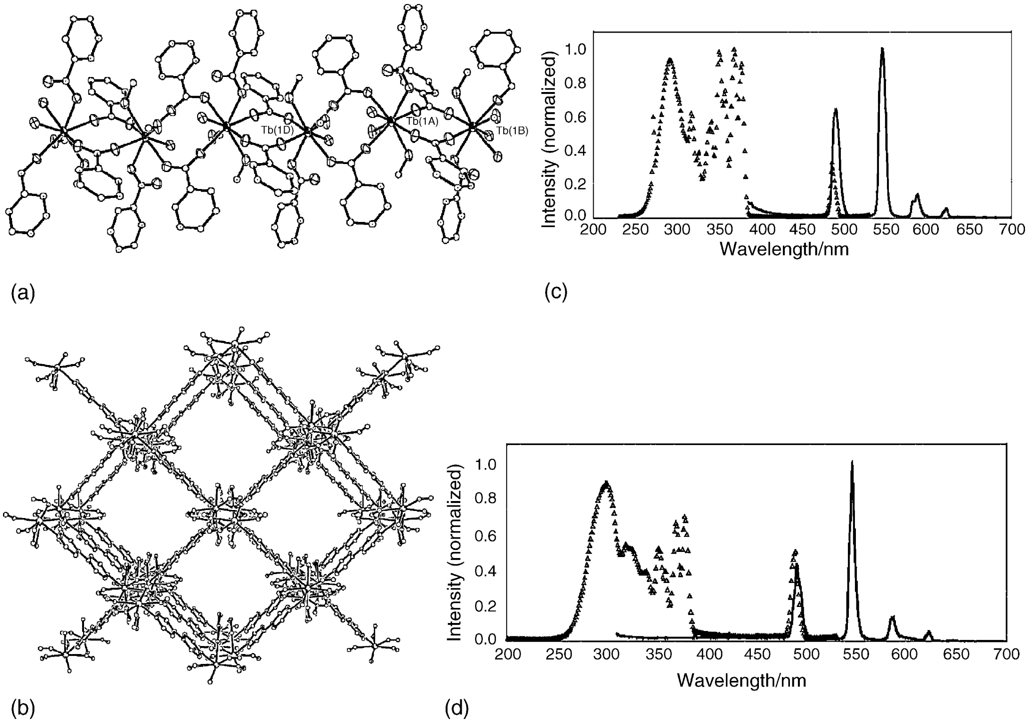


Fig. 54. (a) 1D chain in $\{[Tb(O_2CPh)_3(CH_3OH)_2(H_2O)]\}_n$: the Tb ions are octa-coordinated by the benzoates, the methanol and the water molecules. (b) 3D grid architecture in $\{[Tb_2(O_2CPh)_6(4,4'\text{-bipyridine})]\}_n$: Tb ions and benzoates molecules form 1D chains linked through the bipyridine molecules. (c) Excitation (triangles) and emission (solid line) of $\{[Tb(O_2CPh)_3(CH_3OH)_2(H_2O)]\}_n$; excitation at 300 or 368 nm. (d) Excitation (triangles) and emission (solid line) of $\{[Tb_2(O_2CPh)_6(4,4'\text{-bipyridine})]\}_n$; excitation at 300 nm. Reprinted with permission from Ref. [113]. © 2001 The Royal Society of Chemistry.

In the series of polymers based on AgX (X = PF_6^-, ClO_4^-, OTs^-, NO_3^-, BF_4^-) and 4,4′-dipyridylsulfide (4-PDS), only the compound $\{[Ag(4\text{-}PDS)]OTs\}_n$ has Ag–Ag interactions. No fluorescence is observed for the coordination polymers except for $\{[Ag(4\text{-}PDS)]OTs\}_n$. The band at 600 nm is attributed to the Ag–Ag contact [125].

4.4. Non-linear optical properties

For the construction of non-linear optical (NLO) materials, a non-centrosymmetric arrangement in the solid state is required, and this consists in an interesting challenge. These materials should also contain organic ligands with large molecular first hyperpolarizabilities, β, ideally chromophores with a good electron donor and a good electron acceptor connected through a conjugated bridge. Metal-organic framework building is used to order asymmetric chromophores which are highly dipolar and, due to dipole–dipole repulsions, difficult to align in a non-centrosymmetric way. Some examples of metal-organic frameworks showing frequency conversion (intensity modulation of light: second harmonic generation (SHG) processes) can be found in literature [128–134]. The SHG is studied there by the use of the 1064 nm fundamental wavelength of a Nd:YAG laser using the Kurtz–Perry powder method.

Evans and Lin have outlined strategies to build non-centrosymmetric metal-organic frameworks [133]. They use *p*- or *m*-pyridinecarboxylate linear, rigid and non-symmetric organic ligands as linkers between d^{10} metal ions (Zn^{2+}, Cd^{2+}: tetrahedral or pseudo-tetrahedral) in hydro(solvo)thermal conditions. The building blocks lead to the construction of three-dimensional diamondoid networks or two-dimensional frameworks (Fig. 55a). Even with weak electron donor/acceptor combinations, it is possible to obtain efficiently NLO properties, as the well chosen complexation can allow a good alignment and cooperation between the molecules. The powder SHG intensity of some compounds is comparable or higher than that of technologically important $LiNbO_3$. Furthermore they get a relatively good thermal resistance and are optically transparent. Huang and co-workers synthesize a non-centrosymmetric coordination polymer including the symmetric 4,4′-bipyridine ligand. The compound $\{[Cd_2(4,4'\text{-}bpy)_2(H_2O)_3(SO_4)_2]\cdot 3H_2O\}_n$ crystallizes in the non-centrosymmetric space group *C*2. It consists of one-dimensional chains containing two types of Cd centers coordinated by μ_2- and μ_3-SO_4^{2-} anions and water molecules in the equatorial coordination sites. The chains are connected together with the bipyridine ligands coordinated in the apical sites of the Cd centers (Fig. 55b). This compound shows powder SHG intensity.

However, a remaining problem in the use of such compounds is their poor stability in the laser light.

4.5. Magnetism

Coordination polymers strategy is furthermore employed for the design of molecular-based magnets. Indeed antiferromagnetism, ferrimagnetism and ferromagnetism are cooperative phenomena of the magnetic spins within a solid. They require an interaction or coupling between the spins of the paramagnetic centres. The building of metal-organic frameworks allows the choice of the coupling parameters.

The magnetic coordination polymer has to own a residual permanent magnetization at zero-field for an as high as possible T_c (critical temperature). Its structure should allow parallel coupling of the spins (↑↑↑↑, ferromagnetism) or an antiparallel coupling of inequal spins (↑↓↑↓, ferrimagnetism) of neighbouring paramagnetic spin carriers, so that a non-zero spin of the bulk material results. Some antiparallel couplings of spins (↑↓↑↓, antiferromagnetism) are found in numerous examples as the state of low-spin multiplicity is often more stable than the state of high-spin multiplicity.

An efficient coupling in magnetic materials can occur through open shell organic ligands. Materials with oxo, cyano or azido bridges show a strong coupling between the metal centres and their unpaired electrons. As example, the review of Batten and Murray focuses on the correlation between structures

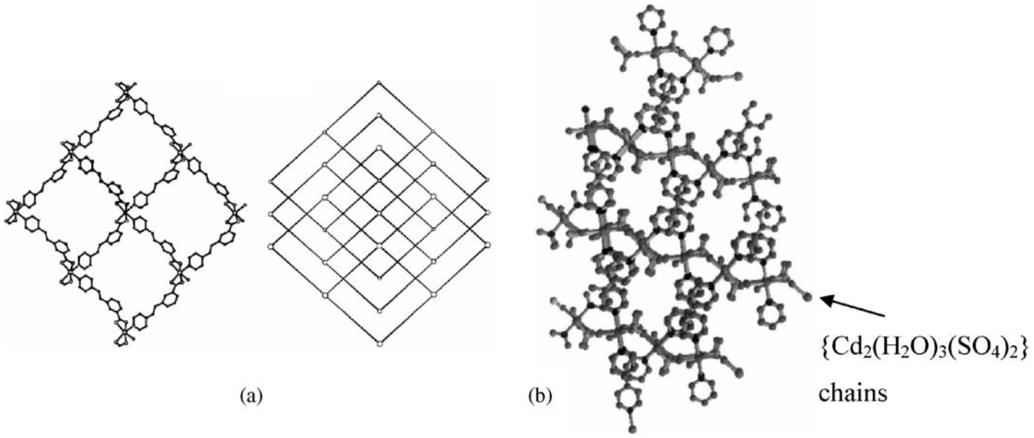


Fig. 55. (a) A example of 2D NLO network: $\{[Cd(3\text{-}(2\text{-}(4\text{-}pyridyl)ethenyl)benzoate)_2]\}_n$ with the interweaving of three independent rhombohedral grids and (b) $\{[Cd_2(4,4'\text{-}bpy)_2(H_2O)_3(SO_4)_2]\cdot 3H_2O\}_n$: the three-dimensional interwoven network. Reprinted with permission from Ref. [133]. © 2002 American Chemical Society.

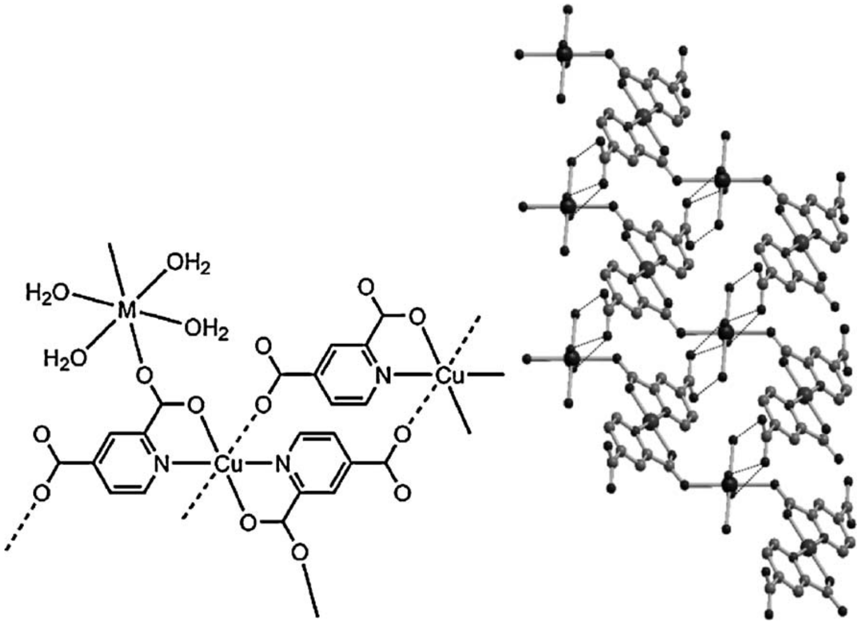


Fig. 56. $\{[Mn([Cu(pyridine\text{-}2,4\text{-}dicarboxylate)])_4(H_2O)_4]\}_n$. Reprinted with permission from Ref. [136]. © 2005 American Chemical Society.

and magnetic properties of coordination polymers containing dicyanamide and tricyanomethanide [135].

Magnetic behaviour is found for coordination polymers built up with carboxylate group containing ligand [136–138]. Mixed metal (Cu^{II}, Mn^{II} or Fe^{II}) two-dimensional coordination polymers exhibit ferromagnetism due to the one-dimensional repeating motif (–M–O–C–O–Cu–O–C–O–M–) [136] (Fig. 56). With the use of such ligands, metal-carboxylate subunits are often formed reinforcing the framework stability and the coupling [139–142]. Zaworotko and co-workers present a scarce example of ferromagnetic coordination polymer ($\{[Cu_2(pyridine)_2(bdc)_2)_3]\}_n$) even at room temperature [142].

The use of ligands with different functionalities is often appropriate to get original crystallographic structures and efficient properties. This is the case with the three-dimensional compound based on the [hydroxy(4-pyridyl)methyl]phosphonate ligand and Ni^{II} ions [143]. The structure is a three-dimensional pillared layered one in which the inorganic layers made up of corner-sharing $\{NiO_5N\}$ octahedra and $\{CPO_3\}$ tetrahedra are connected by pyridyl groups (Fig. 57). This material shows a weak ferromagnetic interaction between the Ni^{II} ions.

Examples of magnetic coordination polymers with polytopic nitrogen-based ligands exist but are much rarer. For instance, the complex $\{[Fe_2(\textit{trans}\text{-}4,4'\text{-azopyridine})_4(NCS)_4]\cdot EtOH\}_n$ presents a temperature dependant magnetic moment due to spin-crossover behaviour [144]. The long ligands avoid or lower the coupling between the metal centres. The complexes $\{[Cu(L_{12})(H_2O)(SO_4)]\cdot 2H_2O\}_n$ and $\{[Co(L_{12})_2(NCS)_2]\cdot 2,5H_2O\}_n$ (L_{12} = 2,5-bis(4-pyridyl)-1,3,4-thiadiazole) show very weak antiferromagnetic coupling [145].

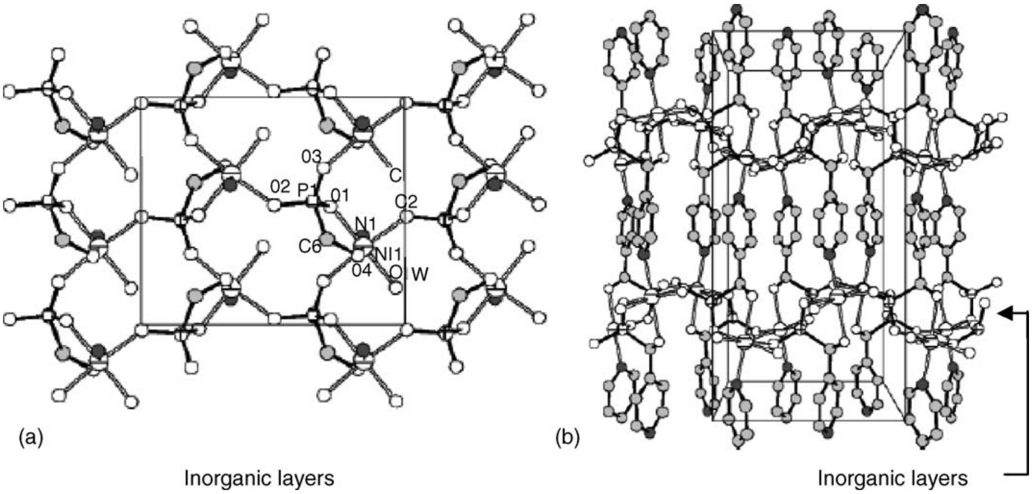


Fig. 57. (a) View of one inorganic layer in $\{[Ni(4\text{-}C_5H_4N)CH(OH)PO_3)(H_2O)]\}_n$ and (b) three-dimensional packing in $\{[Ni(4\text{-}C_5H_4N)CH(OH)PO_3)(H_2O)]\}_n$. Reprinted with permission from Ref. [143]. © 2005 American Chemical Society.

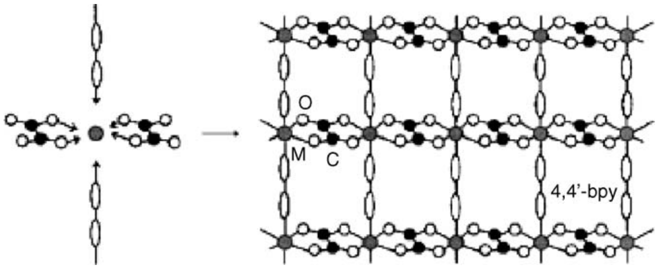


Fig. 58. $\{[\mathrm{M(oxalate)(4,4'\text{-}bipyridine)}]\}_n$. Reprinted with permission from Ref. [139]. © 2004 The Royal Society of Chemistry.

Co-ligands (*N*,*N*-donors and carboxylic) are also used [24]. The carboxylic ligands are used as pillars between metal–*N*-*N*′-donors ligands motifs, allowing the required coupling. The $\{[\mathrm{M(oxalate)(4,4'\text{-}bipyridine)}]\}_n$ ($\mathrm{M = Fe^{II}}$, $\mathrm{Co^{II}}$ or $\mathrm{Ni^{II}}$) (Fig. 58) revealed spontaneous antiferromagnetic ordering, attributed to the strong exchange interactions between the one-dimensional bridged metal ions through oxalate organic ligands and weaker interchain magnetic interactions [146].

Another example of mixed ligands coordination polymer can well illustrate the magnetic behaviour of metal-organic frameworks [147]. The complex $\{[\mathrm{Cu(N_3)_2}((1\text{-}R)\text{-6,6-dimethyl-5,7-methano-2-(2-pyridinyl)-4,5,6,7-tetrahydroquinoline})]\}_n$ presents weak antiferromagnetic interactions between the $\mathrm{Cu^{II}}$ ions through the azide bridge.

In order to allow efficient magnetic coupling, metal ions should be bridged by small ligands allowing short metal–metal contacts. Low-dimensional polymer networks can lead to a final magnetisation within the polymer structure if ferro- or ferrimagnetism can be achieved. Kagomé-lattices in which spin-frustration (inhibition of long-range antiferromagnetic coupling) occurs due to the linking of triangular moieties in two dimensions, are one possibility to realise such a material [148]. In order to avoid anti-ferromagnetic coupling between chains or sheets, further magnetic interaction has to be considered in all three dimensions.

5. Closing remarks

In this review, it was shown how coordination polymer networks can be built to have different dimensionalities, using the rich variety of metal ions given by the periodic table on one hand, and organic molecules with donor atoms, on the other hand. In addition to the diversification of structures due to the combination of shape and size of these building blocks, anions and solvent media also influence the final network. The properties of such polymers range from optical ones to magnetism and can be tuned by choosing the building blocks appropriately. Overall, the concept of coordination polymer networks is therefore a powerful means to generate functional materials. However, even though the primary interactions between ligand and metal ion are now quite well understood, a lot of work remains to be done to gain more insight into the control of the weaker forces that contribute to the solid state structure and which can, in the sum, become non-negligible. This review shows that the secondary interactions, such as H-bonds, metal–metal, metal–π and π–π interactions, are now in the focus of interest, even though they are not easily studied in an isolated way.

Acknowledgments

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