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Coordination Polymers

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ABSTRACT

The chemistry of the field of coordination polymers/metal-organic frameworks (MOFs)/metal-organic coordination networks (MOCNs) has in recent years advanced extensively, affording various architectures, which are constructed from a variety of molecular building blocks with different interactions between them. The development in the field is based on the property investigations in the areas of luminescence, magnetism, catalysis, conductivity, chirality, spin-transition behavior (spin-crossover), non-linear optics (NLO) and zeolitic behavior upon which potential applications of such materials depend.

1. Introduction

Polymers can be defined as high-molecular-weight materials composed of repeating subunits linked by covalent bonds. However, coordination polymers are infinite systems build up with metal ions and organic ligands (called as linkers) as main elementary units linked via coordination bonds and other weak chemical bonds. Such metal-ligand compounds can extend “infinitely” into one, two or three dimensions (1D, 2D or 3D, respectively) *via* more or less covalent metal-ligand bonding. The ligand must be a bridging organic group. At least in one extended dimension the metal atoms must solely be bridged by this organic ligand. These compounds are also named metal organic coordination networks or metal-organic frameworks (MOF) in the case of ordered structures. The arrangement of the components in coordination polymers mostly exist in the solid state only. 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, by self-assembly processes coordination polymers grow via similar interactions (Fig. 1) . 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.

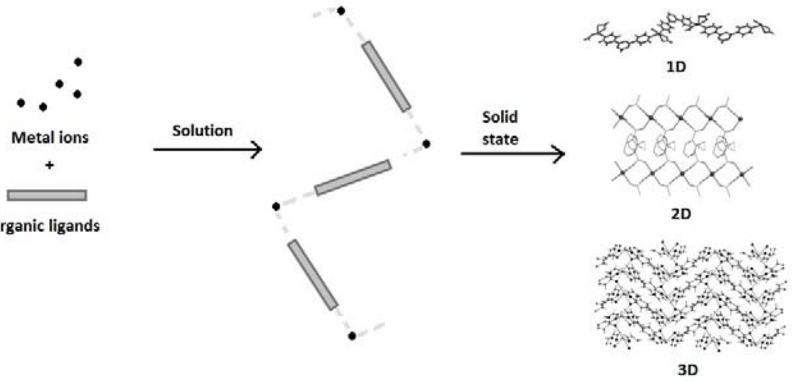


Fig. 1. Formation of coordination polymers

Formation of coordination polymers form building blocks occur mainly via coordination bond. Coordination bonds are formed by 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 charged/polarized donor atom of the ligand. The energy of such interactions is usually evaluated around 50 kJ mol^{-1}. For moderate hydrogen bonds the energy of D-H…A interaction varies between 15-40 kJ mol^{-1} (D-H acts as proton donor to A). The H…A distance is in the range 1.5-2.2 Å for strong O-H…O/N hydrogen bonds with ∠DHA in the range of 140-180° and for weak contacts the distance is between 2-3 Å having ∠DHA 120-180°. π-π interactions play important role in the formation of coordination polymers. Aromatic interactions involve face-to-face (with/without offset) and edge-to-face (C-H…π) orientations. These interactions are the cumulative effect of several factors (electrostatic, van der Walls interaction, repulsion *etc*.) and the aromatic rings are stacked to minimize the repulsion components and maximize attraction. For face-to-face interactions the centroid-to-centroid distance is in the range of 3.4-3.8 Å and the energy for the π-π interaction is 5-10 kJ mol^{-1}.

2. Principles and synthesis

Building blocks

Usually four different kinds of building blocks are used for construction of coordination polymers of higher dimensionality which also contribute to the property of the material.

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

Organic ligands act as bridging organic groups between the metal ions. The ligand molecules have to be multidentate with a minimum of two donor atoms, mostly N-, O- or S-donors to produce extended networks. Ligand molecules may differ from each other in their charges: most used ligands are neutral or anionic. The rigidity/non-rigidity in the bridging ligand plays key role to the structure formation. A list of typical ligands is given in Fig. 2.

Counter ions are present in the structure when neutral ligands are applied. They can influence the environment around the metal ion (more or less coordinating counter ions) and also manipulate 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 by increasing the number of possible weak interactions and can also act as guest molecules in the vacant space in the network. They may play a crucial role when it comes to the construction of highly porous materials.

Dimensionality and motif

The building blocks can be organized by interacting with each other to form coordination polymers with 1D, 2D or 3D structure. Fig. 3 depicts the way of organization of building blocks to form structures of different dimensionalities.

The elementary units are not 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 represent some of the most important known motifs.

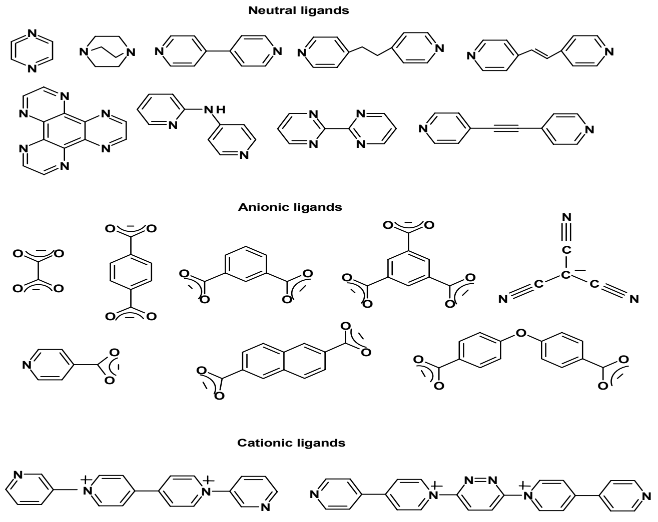


Fig. 2. Typical ligands applied as organic linkers for construction of coordination polymers.

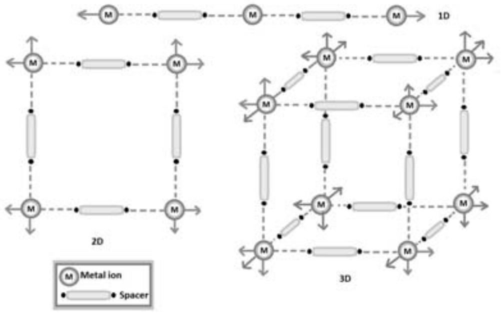


Fig. 3: Organization of building blocks to form structures of different dimensi

onalities.

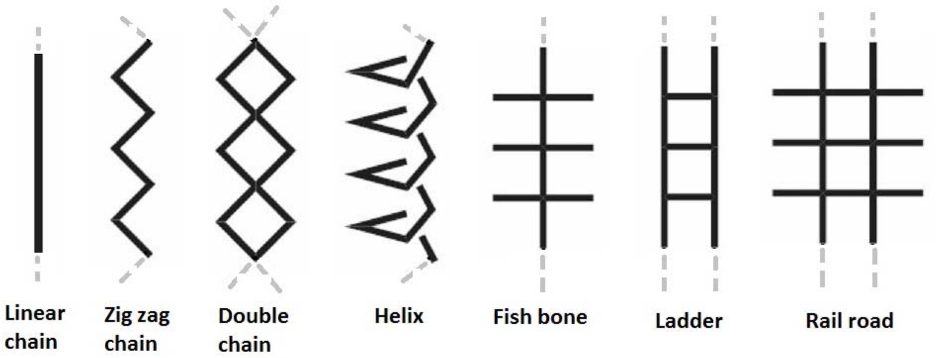


Fig. 4. One-dimensional polymers motif.

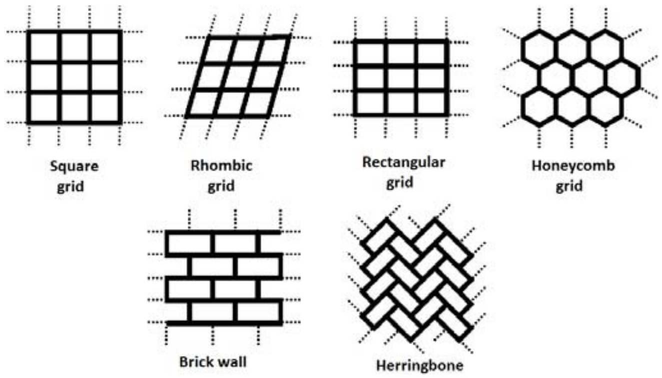
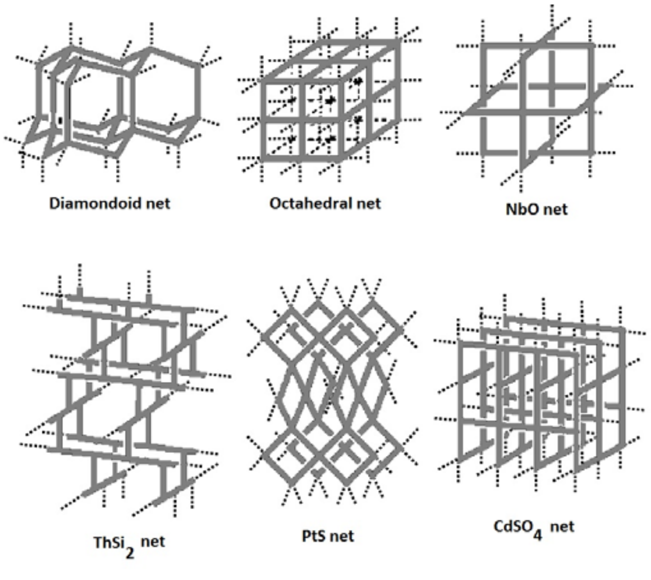


Fig. 5. Motifs in two-dimensional polymers.

Synthesis

To obtain coordination polymers four synthetic strategies are known from literature. Upgrading of synthesis is essential in order to get quality single crystals suitable for X-ray study. It is important to consider that several processes with the same starting materials lead sometimes to different products: isomeric or polymorphic species.

Saturation methods allow the crystal formation from a mixture of the different reagents. In this process crystals grow from the saturated solution by slow evaporation of the mother liquor. Temperature plays important role. 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. Various methods can be applied for such process like solvent liquid diffusion, slow diffusion of reactants etc. Solvothernal synthesis is the most effective method. The running temperature range is usually 120–260° C inside a closed space (autoclave) under autogenous pressure. *Microwave and ultrasonic methods* are so far less used methodsfor the coordination polymer formation.



Diamondoid net **Octahedral net** **NbO net**

$ThSi_2$ net **PtS net** **$CdSO_4$ net**

Fig. 6. Three-dimensional coordination polymers motif.

3. Applications

Coordination polymers are a family of compounds that can be considered as the natural extension of coordination compounds towards polymerization. Their architectures and dimensionalities are defined by the coordinative geometry and capabilities of these two building-blocks. The aim of contemporary coordination polymer chemistry is the development of new crystalline materials having various purposes and possibilities. Even though much effort is still devoted to the preparation and structure determination of a crystalline sample, a final goal is to design properties of the polymeric assemblies of transition metal complexes with applications to material science as luminescence, magnetism, catalysis, conductivity, exchange of anions, adsorption and separation, non linear optical property or application as gas storage materials.

4. Summary

In this mini review it is shown that how coordination polymers can be constructed by using the rich variety of metal ions given by the periodic table and versatile organic molecules having potential donor centers as ligands. Such combination of metal ions and linkers lead to form versatile range of network structures based on 1D, 2D and 3D geometry. 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. Overall, the concept of coordination polymer networks is therefore a powerful means to generate functional materials.

REFERENCES

1. The first use of the term “coordination polymer” may be traced to J. C. Bailar, Jr., 1964, *Preparative Inorganic Reactions*, ed. W. L. Jolly, Interscience, New York, 1, 1–25.
2. C. Janiak, 2003, ‘Engineering of coordination polymers towards applications’, *J. Chem. Soc. Dalton Trans.*, 2781-2804.
3. S. Kitagawa, and S. Noro, 2004, *Compreh. Coord. Chem.* 7, 231-247.
4. A.N. Khlobystov, A.J. Blake, N.R. Champness, D.A. Lemenovskii, A.G. Majouga, N.V. Zyk, and M. Schroder, 2001, ‘Supramolecular design of one-dimensional coordination polymers based on silver(I) complexes of aromatic nitrogen-donor ligands’, *Coord. Chem. Rev.*, 222, 155-192.
5. J. An, S.J. Geib, and N.L. Rosi, 2010, ‘High and Selective CO_2 Uptake in a Cobalt Adeninate Metal−Organic Framework Exhibiting Pyrimidine- and Amino-Decorated Pores, ’ *J. Am. Chem. Soc.,* 132, 38-39.

6. B.H. Ye, M.L. Tong, and X.M. Chen, 2005, ‘Metal-organic molecular architectures with 2,2′-bipyridyl-like and carboxylate ligands’, *Coord. Chem. Rev.*, 249, 545-565.
7. R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R.V. Belosludov, T.C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, and Y. Mita, 2005, ‘Highly controlled acetylene accommodation in a metal−organic microporous material’, *Nature*, 436, 238-241.
8. P.L. Llewellyn, P. Horcajada, G. Maurin, T. Devic, N. Rosenbach, S. Bourrelly, C. Serre, D. Vincent, S. Loera-Serna, Y. Filinchuk, and G. Férey, 2009, ‘Complex Adsorption of Short Linear Alkanes in the Flexible Metal-Organic-Framework MIL-53(Fe)’, *J. Am. Chem. Soc.,* 131, 13002-13004.
9. J.M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, 1995, VCH, New York.
10. A.G. Wong-Foy, A.J. Matzger, and O.M. Yaghi, 2006, ‘Exceptional H_2 Saturation Uptake in Microporous Metal−Organic Frameworks’, *J. Am. Chem. Soc.*, 128, 3494-3495.
11. J. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S. T. Nguyen and J.T. Hupp, 2009, ‘Metal–organic framework materials as catalysts’, *Chem. Soc. Rev.*, 38, 1450-1459.
12. W.J. Rieter, K.M. Pott, K.M.L. Taylor, and W. Lin, 2008, ‘Nanoscale Coordination Polymers for Platinum-Based Anticancer Drug Delivery’, *J. Am. Chem. Soc.,* 130, 11584-11585.
13. Y.Y. Niu, H.G. Zheng, H.W. Hou, and X.Q. Xin, 2004, ‘Heterothiometallic polymeric clusters’, *Coord. Chem. Rev.*, 248, 169-183.
14. X.H. Bu, W. Chen, S.L. Lu, R.H. Zhang, D.Z. Liao, W.M. Shionoya, M. Bu, F. Brisse, and J. Ribas, 2001, ‘Flexible *meso*-Bis(sulfinyl) Ligands as Building Blocks for Copper(II) Coordination Polymers: Cavity Control by Varying the Chain Length of Ligands’, *Angew. Chem., Int. Ed.*, 40, 3201-3203.
15. X.-H. Zhou, Y.-H. Peng, X.-D. Du, C.-F. Wang, J.-L. Zuo, and X.-Z. You, 2009, ‘New 3d−4f Heterometallic Coordination Polymers Based on Pyrazole-Bridged $Cu^{II}Ln^{III}$ Dinuclear Units and Sulfate Anions: Syntheses, Structures, and Magnetic Properties’, *Cryst. Growth Des.*, 9, 1028-1035.
16. J. Tao, J.X. Shi, M.L. Tong, X.X. Zhang, and X.M. Chen, 2001, ‘A New Inorganic−Organic Photoluminescent Material Constructed with Helical $[Zn_3(\mu_3\text{-OH})(\mu_2\text{-OH})]$ Chains’, *Inorg. Chem.*, 40, 6328-6330.
17. J. Tao, M.L. Tong, J.X. Shi, X.M. Chen, and S.W. Ng, 2000, ‘Blue photoluminescent zinc coordination polymers with supertetranuclear cores’, *Chem. Commun.*, 2043-2044.
18. S.R. Batten, B.F. Hoskins, B. Moubaraki, K.S. Murray, and R. Robson, 1999, ‘Crystal structures and magnetic properties of the interpenetrating rutile-related compounds $M(tcm)_2$ [M = octahedral, divalent metal; tcm^- = tricyanomethanide, $C(CN)_3^-$] and the sheet structures of $[M(tcm)_2(EtOH)_2]$ (M = Co or Ni)’, *J. Chem. Soc., Dalton Trans.,* 2977-2986.
19. F. Thétiot, S. Triki, J.S. Pala, and C.J. Gómez-Garcia, 2002, ‘New coordination polymers with a 2,2-dicyano-1-ethoxyethenolate ($dcne^-$) bridging ligand:

syntheses, structural characterisation and magnetic properties of $[M(dcne)_2(H_2O)_2]$ (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II} and Zn^{II}) and $[Cu(dcne)_2(H_2O)]$', *J. Chem. Soc., Dalton Trans.*, 1687-1693.

20. L. Ma, C. Abney, and W. Lin, 2009, 'Enantioselective catalysis with homochiral metal–organic frameworks', *Chem. Soc. Rev.*, 38, 1248-1256, and references therein.
21. D. Sun, R. Cao, J. Weng, M. Hong, and Y. Liang, 2002, 'A novel luminescent 3D polymer containing silver chains formed by ligand unsupported Ag–Ag interactions and organic spacers', *J. Chem. Soc., Dalton Trans.*, 291-292.
22. C.N.R. Rao, A. Ranganathan, V.R. Pedireddi, and A.R. Raju, 2000, 'Novel hybrid layer compound containing silver sheets and an organic spacer ', *Chem. Commun.,* 39-41.
23. Q.-R. Fang, G.-S. Zhu, M. Xue, J.-Y. Sun, and S.-L. Qiu, 2006, 'Porous coordination polymers with zeolite topologies constructed from 4-connected building units', *Dalton Trans*., 2399-2402.
24. X.-M. Zhang, M.-L. Tong, H.K. Lee, and X.-M. Chen, 2001, 'The First Noncluster Vanadium(IV) Coordination Polymers: Solvothermal Syntheses, Crystal Structure, and Ion Exchange', *J. Solid State Chem.,* 160, 118-122.
25. J.-R. Li, R.J. Kuppler, and H.-C. Zhou, 2009, 'Selective gas adsorption and separation in metal–organic frameworks'*Chem. Soc. Rev.,* 38, 1477-1504 and references therein.
26. O.R. Evans, and W. Lin, 2002, 'Crystal Engineering of NLO Materials Based on Metal−Organic Coordination Networks', *Acc. Chem. Res.,* 35, 511-522.
27. L. Pan, D.H. Olson, L.R. Ciemnolonski, R. Heddy, and J. Li, 2006, 'Separation of Hydrocarbons with a Microporous Metal–Organic Framework', *Angew. Chem., Int. Ed.,* 45, 616-619.
28. M. Dinca, A.F. Yu, and J.R. Long, 2006, 'Microporous Metal−Organic Frameworks Incorporating 1,4-Benzeneditetrazolate:□ Syntheses, Structures, and Hydrogen Storage Properties', *J. Am. Chem. Soc*., 128, 8904-8913.