Russian Chemical Reviews **80** (11) 1009 – 1034 (2011) © 2011 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2011v080n11ABEH004193

Homochiral porous metal-organic coordination polymers: synthesis, structure and functional properties †

M P Yutkin, D N Dybtsev, V P Fedin

Contents

I.	Introduction	1009
II.	Methods of synthesis and the structures of metal-organic coordination polymers	1010
III.	Prospects for application	1029
IV.	Conclusion	1031

Abstract. The review concerns the state of the art in and prospects for the development of chemistry of a new class of porous compounds, homochiral metal-organic coordination polymers. Main approaches to the synthesis and structure determination of such systems by X-ray diffraction analysis, as well as stability of metal-organic frameworks and supramolecular chemistry of host – guest inclusion compounds are considered. Prospects for practical application of these compounds first of all for enantioselective resolution and catalysis are discussed. The bibliography includes 175 references.

I. Introduction

Metal-organic coordination polymers (also called metal-organic frameworks, MOF) are crystalline compounds comprising metal ions (or clusters, or polynuclear fragments) coordinated to electrically neutral or negatively charged bridging organic ligands to form one- (1D), two- (2D) or three-dimensional (3D) structures that can be porous. In some cases, porous metal-organic coordination polymers remain sufficiently stable after removal of guest molecules (most often, molecules of solvents used for the synthesis) and can form inclusion compounds with other guests.

M P Yutkin A V Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, prosp. Akad. Lavrentieva 3, 630090 Novosibirsk, Russian Federation. Fax (7-383) 330 94 89, tel. (7-383) 316 58 45, e-mail: yutkin@niic.nsc.ru
D N Dybtsev Pohang University of Sciences and Technology (POSTECH), San 31, 790-784 Hyoja-Dong, Nam-Gu, Pohang, Gyungbuk, Korea. Fax (82-54) 279 20 99, tel. (7-383) 316 58 45,
V P Fedin A V Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, prosp. Akad. Lavrentieva 3, 630090 Novosibirsk, Russian Federation. Fax (7-383) 330 94 89, Department of Sciences, Novosibirsk State University, ul. Pirogova 2, 630090 Novosibirsk, Russian Federation, Fax (7-383) 363 41 83, tel. (7-383) 330 94 90, e-mail: cluster@niic.nsc.ru

Received 10 November 2010
Uspekhi Khimii **80** (11) 1061 – 1086 (2011); translated by A M Raevskiy

Studies on metal-organic coordination polymers represent a relatively new field of interdisciplinary research in the leading laboratories worldwide because the key results were obtained only recently.[1–9] Porous metal-organic coordination polymers exhibit practically valuable properties. Considerable interest in such compounds is due to prospects for wide use of these systems first of all as materials for storage of gases (hydrogen, methane, acetylene, carbon dioxide, *etc.*),[8,10–21] for separation and fine purification of substances[11,22–25] and in catalysis.[5,6,13,19,24,26] It seems there are almost no restrictions on the functional design of such structures based on the laws of coordination chemistry. For instance, by varying the length of organic linkers one can change the size of voids in the frameworks in a targeted manner and increase them to a few nanometres; the hybrid coordination framework can retain its porous structure for an infinite period of time. Recently, considerable advances have been made in the synthesis of porous metal-organic coordination polymers with large specific surface area much exceeding those of nanosized carbon materials or zeolites.[20,27–29] This concerns both microporous (pore diamerer less than 2 nm) and mesoporous (pore diamerer larger than 2 nm) systems.

At present, there has been rapidly increasing interest in chiral highly porous materials. This is first of all due to the need for the design of novel highly efficient enantioselective catalysts and methods for resolution of racemates to obtain optically active compounds. When synthesizing pharmaceuticals, agrochemicals, fragrances and other biologically active compounds, optical purity of products is of paramount importance because biological systems often treat enantiomers as different compounds.

The synthesis of metal-organic coordination polymers from optically pure organic ligands results in homochiral porous metal-organic coordination polymers. In this case, the term 'homochiral' emphasizes that the synthesis is not accompanied by racemization and, therefore, not only some crystals, but also the entire crystalline phase contains

† Dedicated to Academician O M Nefedov on the occasion of his 80th birthday.

identical chiral centres. Such materials are most promising for resolution of optical isomers in racemic mixtures or for heterogeneous enantioselective catalysis because they have stable porous structures and extensive internal surface with regularly arranged chiral organic ligands and inorganic functionalities (*e.g.*, Lewis acid centres and coordinatively unsaturated sites).

There are a number of reviews [30–34] concerning various aspects of the synthesis, structure and functional properties of homochiral metal-organic coordination polymers. However, this field of scientific research has been rapidly developing and new important information appears. In this review, we consider homochiral porous metal-organic coordination polymers reported as to September 2010. We for the first time systematize main approaches to the synthesis of homochiral porous materials. In discussing methods of synthesis the emphasis is placed on the nature of ligands and on the need to synthesize series of isoreticular‡ porous metal-organic coordination polymers. The structures and functional properties of such compounds are considered in detail and examples of their practical application (first of all, in stereoselective sorption and catalysis) are given. The aim of the review is to demonstrate the state-of-the-art in this field of chemical science and to reveal the most promising, from our standpoint, avenues of its development in order to attract the attention of domestic researchers to this class of compounds.

II. Methods of synthesis and the structures of metal-organic coordination polymers

Metal-organic coordination polymers are synthesized in solutions of corresponding metal salts and organic ligands at room temperature or on heating. If the temperature of a reaction is higher than the boiling point of the solvent, the reaction is carried out in sealed tubes (autoclaves). In addition to water, the most popular solvents include alcohols, carboxylic acid dialkylamides [*N*,*N*-dimethylformamide, *N*,*N*-diethylformamide (DEF), *N*,*N*-dimethylacetamide (DMA)] and pyridine (Py). Usually, salts of di- or trivalent first-row transition metals are used because coordination chemistry of these metals has been well studied.

By varying the reaction conditions one can obtain different products starting from the same initial compounds. In most cases, the influence of various parameters (nature of solvent, temperature, reactant ratio, reaction time) on the synthesis of metal-organic coordination polymers is specific to each particular system and is still to be clarified. Thus, the synthesis conditions of these compounds can vary over a wide range and obtaining pure crystalline phase is a complicated task.

Various physicochemical methods are used for characterization of the polymers in question. These first of all include single crystal X-ray diffraction and powder X-ray diffraction (PXRD) for the determination of the crystal structure and the phase composition of samples. Since guest molecules can be highly disordered, X-ray data are often insufficient and one should use elemental analysis, thermogravimetric analysis (TGA) as well as IR and NMR spectroscopies.

An important property of porous compounds is the structural stability upon removal of guest molecules. If a porous compound with unoccupied voids exhibits reversible physisorption of gases and the specific surface area and pore volume determined from physisorption data are equal or close to theoretical values, it is called permanently porous. Research on permanently porous compounds involves studies on the sorption properties and evaluation of the internal surface areas, pore sizes, pore volumes and the guest-accessible volumes. If the framework of a compound is unstable in the absence of guest molecules but can be stabilized by molecules of other compounds, the pore size and the accessible volume are calculated from structural data.

Depending on the presence or absence of covalent bonds between structural units in the crystal, compounds are divided into island, chain, layered and framework ones.[35] Porous metal-organic coordination polymers are usually treated as having framework structures. However, it is not infrequent that a porous structure is formed involving various supramolecular interactions between coordination motifs of lower dimensionality. In the text below, the crystal structures of coordination polymers will be discussed without distinguishing between compounds whose frameworks are formed through supramolecular or only coordination interactions.

1. Metal-organic coordination polymers containing rigid chiral bridging ligands

At present, the most widely used approach to the synthesis of homochiral metal-organic coordination polymers involves the use of chiral organic ligands playing the role of rigid bridges (linkers) to make the framework structure porous (Fig. 1).

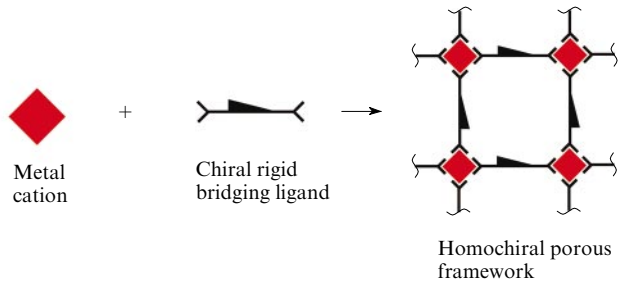


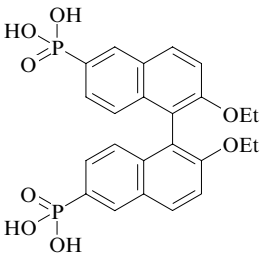
Figure 1. Synthesis using a chiral rigid bridging ligand: a scheme.

A key drawback of this approach is that the appropriately long, rigid, optically pure organic ligands are usually hardly accessible. Homochiral metal-organic coordination polymers include a large group of compounds synthesized using optically active 1,1′-binaphthyl derivatives.

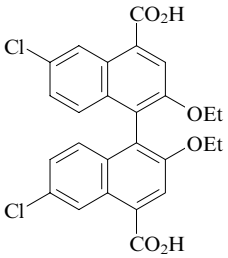
a. Coordination polymers based on 1,1′-binaphthyl derivatives

Compounds **1** of the general formula $[Ln(H_2L1)(H_3L1).(H_2O)_4]\cdot x\,H_2O$ (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb; $x = 9-14$) were obtained by slow evaporation of solutions of corresponding lanthanide nitrates or perchlorates and 2,2′-diethoxy-1,1′-binaphthyl-6,6′-diphosphonic acid (H_4L1) in methanol.[36]

‡ Porous metal-organic coordination polymers with different-length bridging organic ligands having the same fashion of binding metal centres and the same topology but different geometric parameters of the metal-organic framework are called isoreticular.[4]



H_4L1



H_2L2

X-Ray diffraction data were only reported for the structure with Ln = Gd, while PXRD data were used to prove that all compounds are isostructural. According to X-ray diffraction data, the gadolinium compound forms corrugated layers (Fig. 2) with an interplanar distance of about 12 Å. Analysis of the PXRD data suggested that removal of guest molecules leads to distortion of the long-range lamellar-type structure of compounds **1**; however, it can be recovered upon treatment of the crystals with water vapour. The sorption and catalytic properties of compounds **1** were investigated (Section III).

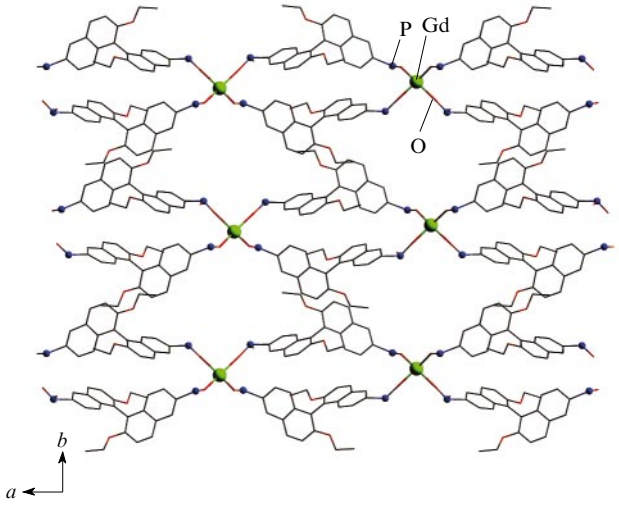


Figure 2. Structure of a layer in compounds **1**.[36]
The bound water molecules are omitted.

Reactions of ligand H_4L1 with transition metal salts in alcoholic or alcoholic aqueous soltions result in corresponding homochiral metal-organic coordination polymers.[37] The structure of compound $[Mn(H_2L1)(MeOH)]\cdot MeOH$ (**2**) contains coordination chains linked to form a framework (Fig. 3) with a channel cross section of 5×3 Å. Compound $[Co_2(H_2L1)_2(H_2O)_3]\cdot 4\,H_2O$ (**3**) has a framework structure too. As in the preceding case, it is built of chains linked by binaphthyl ligands (Fig. 4). Channels in the structure of compound **3** have a size of 3×4 Å. Based on the X-ray diffraction data, it was suggested [37] that compounds **2** and **3** have porous structures; however, the framework stabilities were not studied experimentally.

Three homochiral porous metal-organic coordination polymers based on lanthanides (Gd, Er, Sm) and optically pure 6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthyl-4,4′-dicarboxylic acid (H_2L2) with the general formula $[Ln_2(L2)_3.(def)_2(py)_2]\cdot 2\,DEF\cdot 5\,H_2O$ (**4**) were reported (Ref. 38).§

§ Hereafter, the abbreviation of the solvent whose molecules are coordinated to the metal is given by the corresponding lower-case letters.

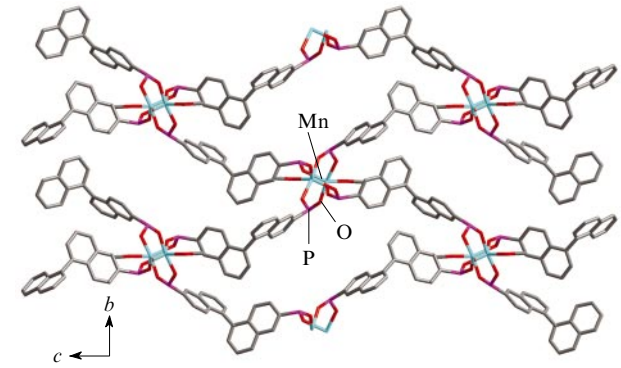


Figure 3. View of the 3D framework $[Mn(H_2L1)(MeOH)]$ of compound **2**.[37]

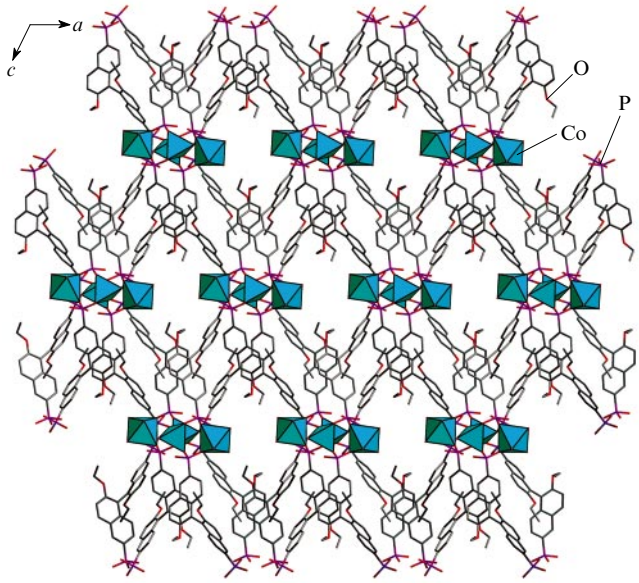


Figure 4. View of the 3D framework $[Co_2(H_2L1)_2(H_2O)_3]$ of compound **3**.[37]

According to X-ray diffraction data, binaphthyl ligands link metal cations to form 2D networks with the 6^3 topology (honeycombs). The interpenetrating networks form a framework with the $\{4^9; 6^3\}$ topology and a channel cross-section of 3×6 Å.

Reactions of transition metal nitrates or perchlorates with H_2L2 result in coordination polymers **5** of the general formula $[M_2(H_2O)(L2)_2(py)_3(dmf)]\cdot DMF\cdot x\,H_2O$ ($x = 2$, M = Mn; $x = 3$: M = Co, Ni).[39] Analysis of the X-ray single crystal and power diffraction showed that these compounds are isostructural and bulit of tetragonal grids (Fig. 5) that stack on top of each other in a staggered fashion along the *a* axis. Adjacent layers are shifted by 0.5 translation along the *b* and *c* axes, respectively, and have an interlayer separation of 7.5 Å. As a consequence, these compounds have a small void space, which is occupied by *N*,*N*-dimethylformamide and water molecules. No stability studies of the compounds with respect to removal of guests were carried out.

Layered lanthanide phosphonates based on crown-containing binaphthyl derivatives of the general formula

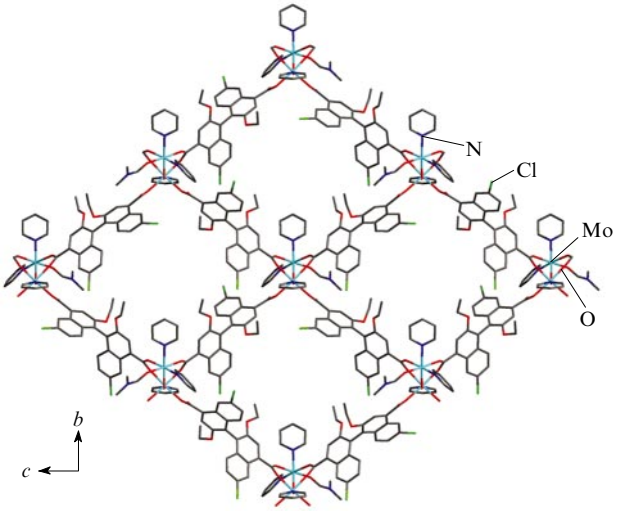


Figure 5. View of 2D grid in the structures of compounds **5**.[39] The DMF and water guest molecules are omitted.

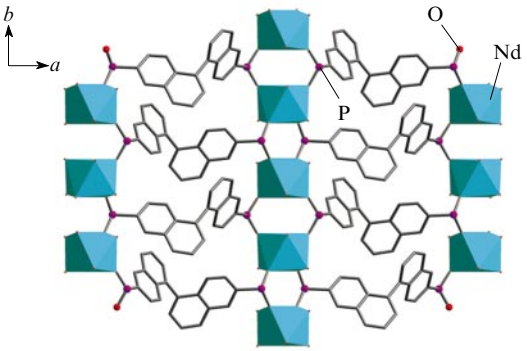
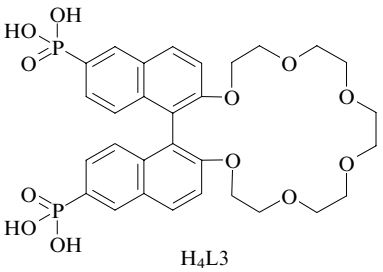
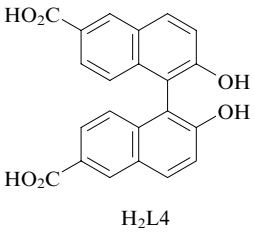


Figure 6. Structure of $[Nd_2(HL3)_2(MeOH)_8]$ layer in compound **6** (Ln = Nd).[40] Shown are only the donor oxygen atoms of methanol; the crown ether fragments are omitted for simplicity.

$[Ln_2(HL3)_2(MeOH)_8]\cdot H_4L3\cdot 3\,HCl\cdot 6\,H_2O$ (Ln = Sm, Nd; **6**) were synthesized.[40] Polymers **6** are isostructural and have a layered structure (Fig. 6). The interlayer space is filled with guest water and H_4L3 molecules, as well as by chloride anions and solvated protons. The compounds retan their crystal structures upon removal of the guest molecules.



H_4L3



H_2L4

Metal-organic coordination polymers $[Mn(L4)(def)_2\cdot(MeOH)]\cdot Lut$ (**7**), $[Co(L4)(def)(H_2O)]\cdot Lut\cdot DEF$ (**8**), $[Cd(L4)(py)_3]\cdot Py\cdot H_2O$ (**9**) and $(Me_3HN)_2[Cd_2Cl_2(L4)_2]\cdot 6\,H_2O$ (**10**) (Lut is lutidine) were synthesized by heating the corresponding metal salts and 2,2′-dihydroxy-1,1′-binaphthyl-6,6′-dicarboxylic acid in *N*,*N*-diethylformamide at 25–60 °C.[41]

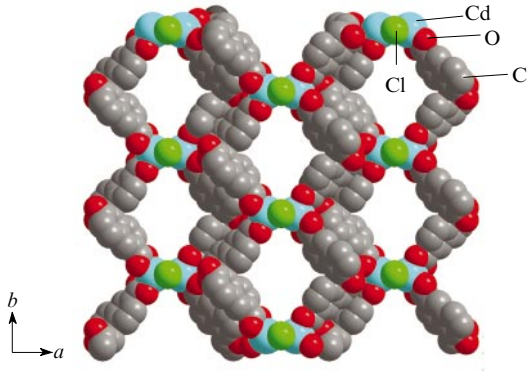


Figure 7. View of the framework $[Cd_2Cl_2(L4)_2]^{2+}$ of compound **10**.[41]

Zig-zag chains in the crystals of compounds **7** and **8** form corrugated layers involving hydrogen bonds. The layers are shifted by half the translation period and stack on top of each other with an interlayer separation of 13 Å. The void space between the layers is occupied by guest molecules. The framework in $[Cd(L4)(py)_3]\cdot Py\cdot H_2O$ (**9**) is formed by helical chains linked by hydrogen bonds. Compound **10** is built of chains of the general formula $[Cd_2Cl_2(L4)_2]$ also linked by hydrogen bonds to form a framework (Fig. 7). Here, an important structural feature is the presence of voids 11×12 Å in size. The viod space is 59%. Channels are filled with Me_3HN^+ cations and water molecules. Compounds **7** and **8** exposed to vacuum at elevated temperatures lose the guest molecules; this leads to collapse of their frameworks, as was proved by PXRD. Contrary to this, removal of guest molecules from the frameworks of the cadmium compounds **9** and **10** has no effect on their crystal structures.

Compound $[Cu_2(L4)_2(H_2O)_2]\cdot 2\,MeOH\cdot 4\,H_2O$ (**11**) was obtained by slow diffusion of *N*,*N*-dimethylaniline to a solution of copper nitrate and H_2L4 in a water/methanol mixture at room temperature.[42] Copper(II) cations form 'paddle-wheel' type dimers. In the crystal structure, dinuclear fragments $Cu_2(L4)_4$ are linked by bridging binaphthyl ligands to form hydrogen bonded chains. The space between the chains is occupied by guest water and methanol molecules. The guest-accessible volume is 49%. Also, compound $(Et_2MeHN)_2[Zn(L4)_2(H_2O)_2]\cdot 2\,MeOH\cdot 4\,H_2O$ (**12**) was synthesized by heating zinc nitrate, H_2L4 and *N*,*N*-dimethylaniline in a diethylformamide/methanol mixture at 50 °C. Compound **12** has a layered structure. Layers are shifted by half the translation period in the *ab* plane (Fig. 8). In addition to the guest water and methanol molecules the interlayer space is filled with Et_2MeHN^+ cations. Polymers **11** and **12** exposed to vacuum lose the guest solvent molecules but retain their crystal structures, as was confirmed by PXRD data. Subsequent treatment with water vapour and alcohol is accompanied by sorption of two alcohol molecules and four water molecules per formula unit.

Homochiral metal-organic coordination polymers were also synthesized using the *S*-enantiomer of 2,2′-dimethoxy-6,6′-bis[2-(4-pyridyl)ethenyl]-1,1′-binaphthyl (L5).[43]

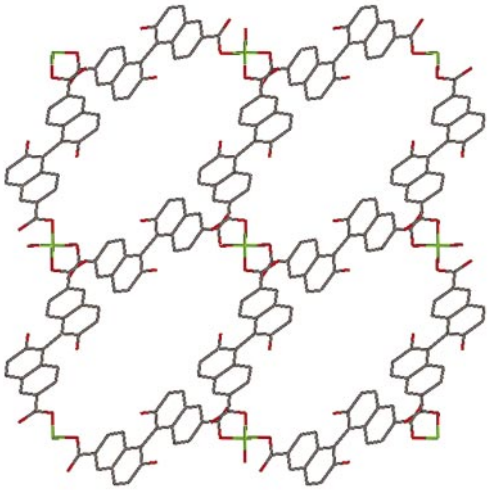
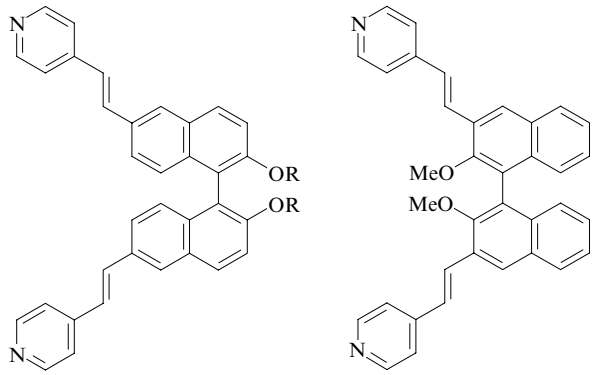


Figure 8. View of the 2D grid $[Zn(L4)_2(H_2O)_2]$ of compound **12** down the *c* axis.[42]



L8

R = Me (L5), Et (L6);
R–R = $(CH_2CH_2O)_4(CH_2)_2$ (L7).

The structures of six coordination polymers (including porous systems) based on the first- and second-row transition metal cations were reported. Single crystals of all compounds were obtained by slow diffusion of diethyl ether to a solution of corresponding metal salt and the ligand L5. Compound $[Ni(L5)_2Cl_2]\cdot 3\,EtOH\cdot 4\,H_2O$ (**13**) is built of $[Ni(L5)_2Cl_2]$ chains that form layers through supramolecular interactions and then a porous framework stable up to 250 °C (Fig. 9). The channel cross-section in this compound is 6×17.5 Å in size.

In the structure of compound $[Cu_2(L5)_4(H_2O)(dmf)_2].(ClO_4)\cdot DMF\cdot 8\,EtOH\cdot 3\,H_2O$ (**14**), there are two crystallographically independent copper cations with different coordination polyhedra (a tetrahedron and an octahedron) and two types of chains. Layers of the two types of chains form stacks held together through supramolecular interactions (Fig. 10). Channels in this metal-organic coordination polymer have a cross-section of 16×37 Å. Voids are filled with guest solvent molecules and perchlorate anions. The void space is 52% and the framework is stable to 180 °C.

The framework structure of $[Cu(L5)_2(H_2O)_2].(NO_3)_2\cdot 2\,DMF\cdot 2\,MeOH\cdot 6\,H_2O$ (**15**) is formed by coordination chains. The molecular framework of compound **15** has channels 11×15 Å in size and is stable up to 165 °C. After removal of guest molecules, the void space of the framework is 45%. Compounds $[Cd(L5)_2(H_2O)_2](ClO_4)_2\cdot 1.5\,DMF\cdot 1.5\,EtOH\cdot 1.5\,H_2O$ (**16**), $[Co(L5)_2(H_2O)_2].(ClO_4)_2\cdot 1.5\,DMF\cdot 2\,MeCN\cdot 3\,H_2O$ (**17**) and $[Mn(L5)_2.(MeCN)(H_2O)](ClO_4)\cdot 2\,MeCN\cdot 2.5\,MeOH\cdot 2.5\,H_2O$ (**18**) are isostructural. They are built of tetragonal layers stabilized by supramolecular interactions. The frameworks of compounds **16**–**18** have channels 8 Å in diameter and are stable to nearly 200 °C.

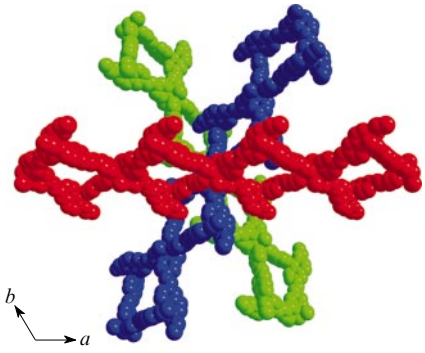


Figure 9. Structural fragment $[Ni(L5)_2Cl_2]$ of compound **13**.[43] The chains shown in different colour form layers stacked in the ABCABC... fashion.

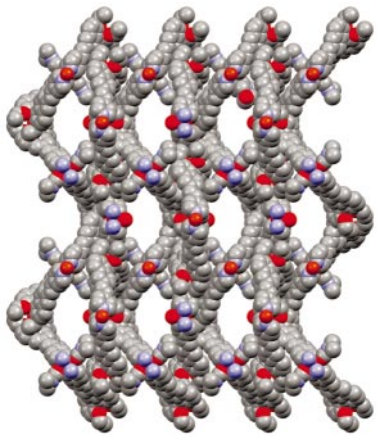


Figure 10. View of the framework $[Cu_2(L5)_4(H_2O)(dmf)_2]$ of compound **14**.[43]
Shown are only the donor atoms of DMF and water.

Heating of a solution of $[Ni(acac)_2(H_2O)_2]$ (acac is acetylacetonate) with 6,6′-bis[2-(4-pyridyl)ethenyl]-2,2′-diethoxy-1,1′-binaphthyl (L6) and its crown-containing analogue L7 in a $MeCN-CH_2Cl_2$ mixture affords compounds $[Ni(acac)_2(L6)]\cdot 3\,MeCN\cdot 6\,H_2O$ (**19**) and $[Ni(acac)_2.(L7)]\cdot 2\,MeCN\cdot 5\,H_2O$ (**20**), respectively.[44] The frameworks of compounds **19** and **20** are stabilized by π–π interactions between the binaphthyl and pyridine rings (Fig. 11) and contain two types of channels. One type of channels has a cross-section of 17×17 Å and is occupied by water and acetonitrile molecules, whereas the other one has a cross-section of 7×11 Å and is filled by water molecules only. The void space is 46% (**19**) and 40% (**20**). TGA and PXRD studies of these compounds showed no loss of crystallinity after complete elimination of guest water and acetonitrile molecules.

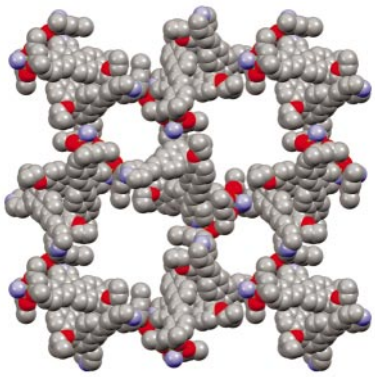


Figure 11. View of the framework $[Ni(acac)_2(L6)]$ of compound **19**.[44]

Yet another polymer, $[Cd(L8)(dmf)_4](ClO_4)_2 \cdot EtOH \cdot 0.5\,H_2O$ (**21**), was obtained by slow diffusion of diethyl ether to a solution of cadmium nitrate and the *S*-enantiomer of ligand L8 in a DMF – *o*-$Cl_2C_6H_4$ – EtOH mixture.[45] The structure of compound **21** comprises stacks of zig-zag chains stabilized by π – π interaction between binaphthyl rings (Fig. 12). There are channels with a cross-section of 8×9 Å; the void space is 32%. According to PXRD data, removal of guest molecules from compound **21** on heating *in vacuo* leads to loss of the long-range order.

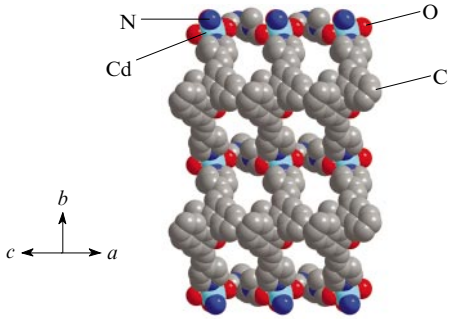


Figure 12. View of the framework $[Cd(L8)(dmf)_4]^{2+}$ of compound **21**.[45]
Shown are only the donor oxygen atoms of DMF molecules.

Heating of a solution of cadmium perchlorate and ligand L8 in the system DMF – *o*-$Cl_2C_6H_4$ – EtOH at 70 °C gives a coordination polymer $[Cd(L8)_2(ClO_4)_2] \cdot 3\,EtOH \cdot 6\,H_2O$ (**22**). Under similar conditions, the addition of a small amount of water to the reaction mixture led to compound $[Cd(L8)_2(ClO_4)(H_2O)](ClO_4) \cdot 1.5\,(o\text{-}Cl_2C_6H_4) \cdot 3\,EtOH \cdot 6\,H_2O$ (**23**). Both metal-organic coordination polymers have porous frameworks built of chains (Fig. 13). The framework structures contain one type of channels with a cross section of 10×12 Å for compound **22** and two types of channels with cross sections of 8×16 Å (along the *a* axis) and 6.5×16.5 Å (along the [110] direction) for compound **23**. The void space is 45% (**22**) and 48% (**23**). Analysis of XPA data showed that removal of guest molecules causes both compounds to lose their long-range order, thus indicating structural instability. However, subsequent treatment with ethanol vapours leads to restoration of the crystal structure.

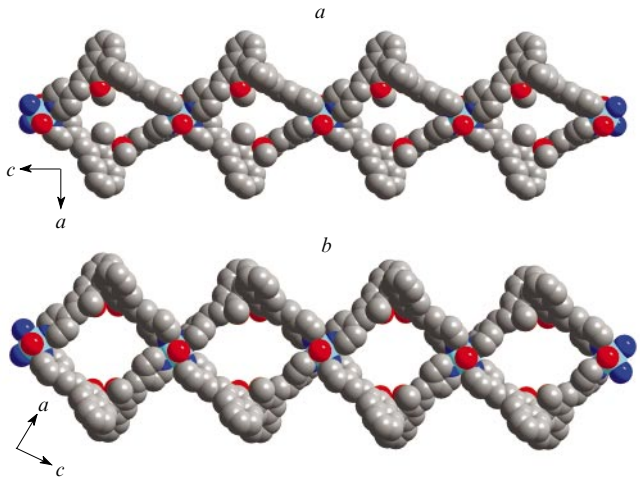


Figure 13. Polymeric chains $[Cd(L8)_2(ClO_4)_2]$ of compound **22** (*a*) and $[Cd(L8)_2(ClO_4)(H_2O)]$ of compound **23** (*b*).[45]
Shown are only the donor oxygen atoms of perchlorate anions.

In the compound $[Cd(L8)_2(ClO_4)_2] \cdot 11\,EtOH \cdot 6\,H_2O$ (**24**),[46] the binaphthyl ligands L7 link cadmium ions to form chains stabilized by strong π – π stacking interaction. This compound crystallizes in the hexagonal chiral space group (Fig. 14). Pseudohexagonal channels are 17 Å in diameter and the void space is 54%. Compound **24** retains its long-range order upon removal of guest molecules *in vacuo*, as was confirmed by gas sorption studies.

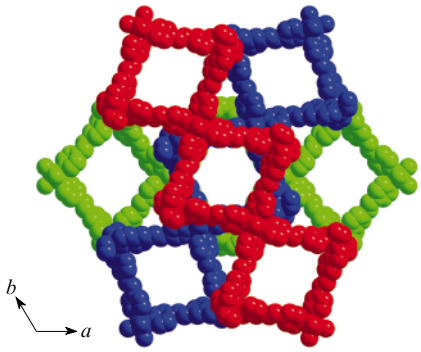
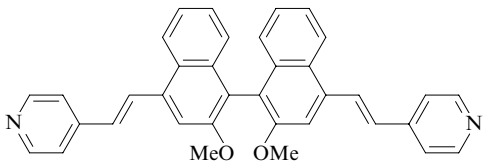


Figure 14. View of the framework $[Cd(L8)_2(ClO_4)_2]$ of compound **24**.[46]
The framework-forming coordination chains are shown in different colours.

The structures and properties of six coordination polymers obtained using the *S*-enantiomer of the ligand L9 were reported.[47]



L9

Their frameworks differ to some extent in the structure and nature of the ligands that complete the coordination

polyhedra of the metal ions. For instance, in $[Cd_2(L9)_4(dmf)(ClO_4)(H_2O)_2](ClO_4)_3 \cdot DMF \cdot 3\,MeCN \cdot 6\,H_2O$ (**25**) the coordination chains form layers. The layers are packed in an ABAB fashion, being held together by strong $\pi-\pi$ interaction between binaphthyl rings, which leads to formation of channels with cross-sections of 10×10 and 7×8 Å. The guest-accessible volume is 40%. The structure of $[Cd(L9)_2(NO_3)_2] \cdot DMF \cdot 2\,EtOH \cdot 2.5\,H_2O$ (**26**) is comprised of layered fragments (Fig. 15). The layers obey the ABAB packing motif and are noticeably shifted relative to one another in the *ab* plane; consequently, channels with a cross-section of 11×16.5 Å are formed. The guest-accessible volume is 30%. Compound $[Ni(L9)_2Cl_2] \cdot DMF \cdot 4\,EtOH \cdot H_2O$ (**27**) isostructural to the cadmium derivative **26** (see above) has channels with a cross-section of 12×16.5 Å and a void space of 35%.

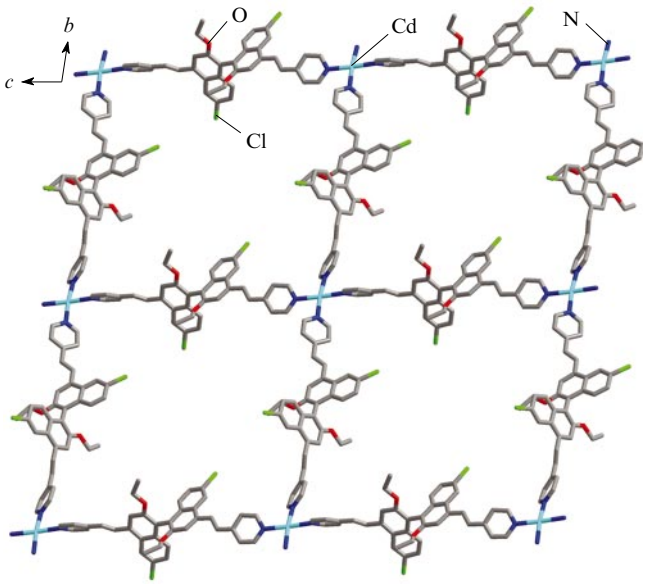
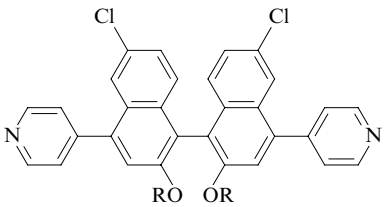


Figure 15. A schematic view of the structural fragment $[Cd(L9)_2(NO_3)_2]$ of compound **26**.[47]

The coordination polymer $[Cd_3Cl_6(L10)_3] \cdot 4\,DMF \cdot 6\,MeOH \cdot 3\,H_2O$ (**28**) was obtained by slow diffusion of diethyl ether in a solution of (*R*)-2,2′-dihydroxy-4,4′-bis(4-pyridyl)-6,6′-dichloro-1,1′-binaphthyl (L10) and $CdCl_2$ in a MeOH – DMF mixture.[48]



R = H (L10), Et (L11).

According to X-ray data, the structure of this polymer contains chain fragments $[Cd_2(\mu\text{-}Cl)_2]$ linked by the bridging ligands L10 to form a framework (Fig. 16). The channels in the framework have a cross-section of 16×18 Å are are occupied by guest solvent molecules. The void space is ~54%. Based on the XPA and gas sorption data, it was concluded that the framework of the metal-organic coordination polymer is stable after removal of guest molecules.

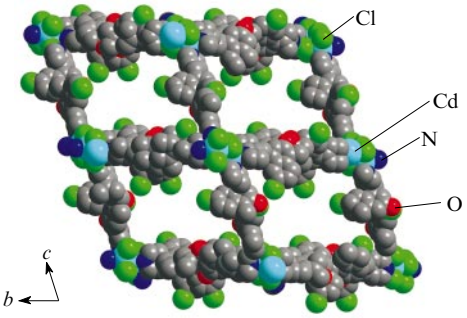


Figure 16. View of the framework $[Cd_3Cl_6(L10)_3]$ of compound **28**.[48]

Compound $[Cd(L11)_2(H_2O)_2](ClO_4)_2 \cdot 2\,DMF \cdot 3\,EtOH \cdot 5\,H_2O$ (L11 is (*R*)-4,4′-bis(4-pyridyl)-6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthyl) (**29**) has a complex 3D structure formed by three interpenetrating networks.[49] In spite of a high degree of interpenetration, it contains two types of large voids with cross-sections of 20×39 and 20×20 Å. Compound **29** retains its long-range order on heating to 160 °C. This was confirmed by the powder X-ray diffraction patterns and CO_2 sorption studies.

Two homochiral porous metal-organic coordination polymers based on derivatives of binaphthyl L11 were synthesized.[50] In the structure of $[Cd_3(L11)_4(NO_3)_6] \cdot 7\,MeOH \cdot 5\,H_2O$ (**30**), there are two clearly seen structure-forming units, *viz*., a layered fragment formed by cadmium cations and the binaphthyl ligand and a chain fragment. The layers and chains are linked by bridging nitrate anions to form an open framework. Channels with a cross-section of 13.5×13.5 Å are occupied by guest molecules. The guest-accessible volume is 53%. The framework of $[Cd(L11)_2(H_2O)_2](ClO_4)_2 \cdot DMF \cdot 4\,MeOH \cdot 3\,H_2O$ (**31**) is formed by two interpenetrating 2D networks, which leads to formation of rather large voids (Fig. 17). Channels in this framework have a cross-section of 12×15 Å and the void space is 59%. Such compounds retain their long-range order upon complete elimination of guest molecules and are characterized by noticeable gas sorption.

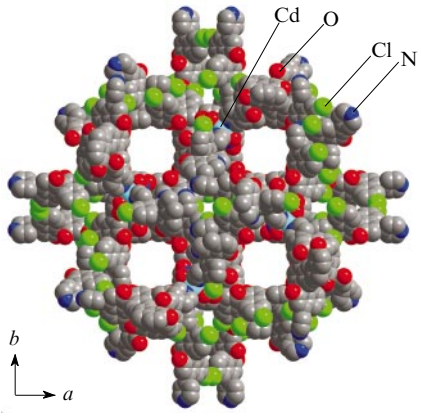
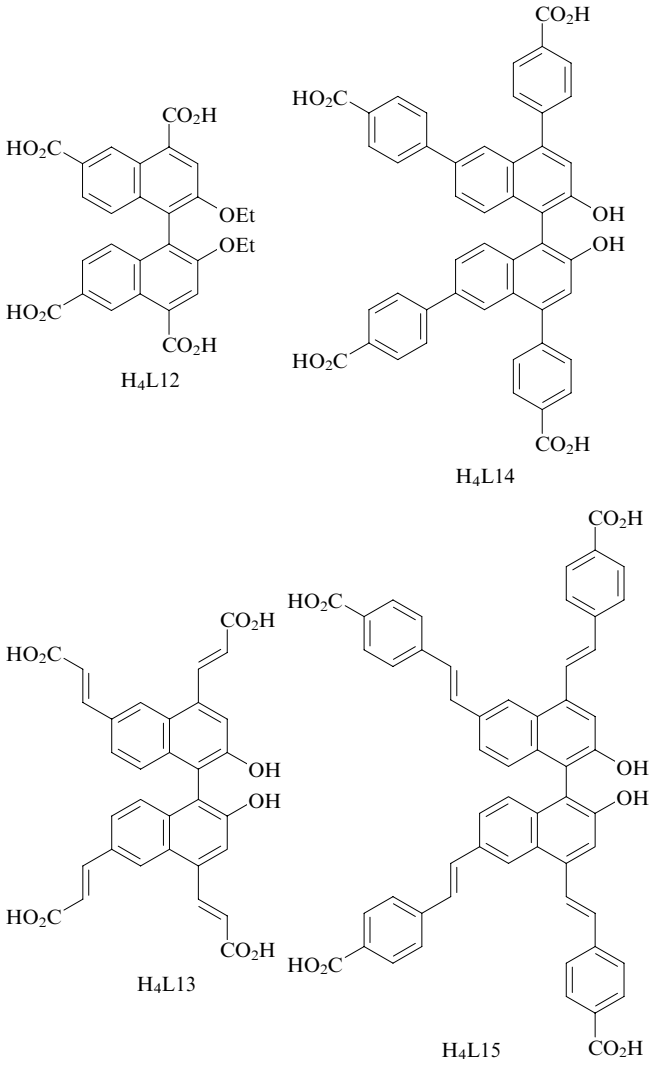


Figure 17. View of the framework $[Cd(L11)_2(H_2O)_2]^{2+}$ of compound **31**.[50]



A number of homochiral porous metal-organic coordination polymers of copper based on 2,2′-diethoxy-1,1′-binaphthyl-4,4′,6,6′-tetracarboxylic acid (H_4L12) were synthesized.[51, 52]

Compounds $[Cu_2((R)\text{-L12})(H_2O)_2]\cdot 12\,DEF\cdot 16\,H_2O$ (**32**) and *rac*-$[Cu_2(L12)(H_2O)_2]\cdot 8\,DMF\cdot 4\,H_2O$ (**33**) have omplex 3D structures and a unique $\{4^3; 6^2; 8\}$ topology (Fig. 18). It should be emphasized that these frameworks are interrelated not only as an *R*-enantiomer and a racemate, but are also catenation isomers, *i.e.*, the framework of compound **33** comprises two interpenetrating networks, $[Cu_2((R)\text{-L12})(H_2O)_2]$ and $[Cu_2((S)\text{-L12})(H_2O)_2]$. Computer simulation showed that interpenetration of two frameworks of the same chirality is geometrically impossible. This is the first example of ligand-chirality controlled framework interpenetration. Compound **32** has a very large guest-accessible volume of 85%. Channels in this compound have a cross-section of 32×15 Å. The channel cross-section in racemate **33** is somewhat smaller, 14×14 Å, due to interpenetration. The framework stability of compounds **32** and **33** to removal of guest molecules was studied. Dried samples were characterized by much smaller specific sirface area compared to that calculated from structural data; this suggests partial collapse of the metal-organic framework.

Reaction of copper(II) nitrate with optically pure ligand H_4L12 in a DMF/water mixture in the presence of ammonia results in the metal-organic coordination polymer $[Cu_2((R)\text{-L12})(dmf)_2][Cu((R)\text{-}H_2L12)(H_2O)]\cdot 13\,DMF\cdot 10\,H_2O$ (**34**) with unusual structure.[52] The framework of this compounds can be described as a 3D network $[Cu_2((R)\text{-L12})(dmf)_2]$ with the $\{4^3; 6^2; 8\}$ topology (as in $[Cu_2((R)\text{-L12})(H_2O)_2]$) interlocked with 2D $[Cu((R)\text{-}H_2L12)(H_2O)]$ grids. As a result of interlocking, structure **34** contains two types of channels 11 and 6 Å in diameter; the void space is 59%. A similar reaction with the racemic ligand H_4L12 results in compound $[Cu_2((R)\text{-L12})(dmf)_2][Cu_2((S)\text{-L12})(dmf)(\mu\text{-}H_2O)_{0.5}]\cdot 14\,DMF\cdot 9\,H_2O$ (**35**) which also has a framework structure with channels 12 and 6 Å in diameter and a void volume of 58%. An analysis of nitrogen sorption data suggests that structures **34** and **35** retain their long-range order upon removal of guest solvent molecules, probably due to framework interpenetration (Fig. 19 *a*).

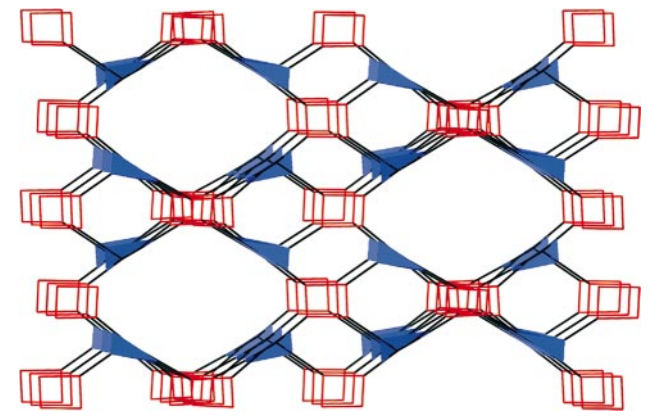


Figure 18. Schematic representation of the framework $[Cu_2((R)\text{-L12})(H_2O)_2]$ of compounds **32**, **33**.[51, 52]

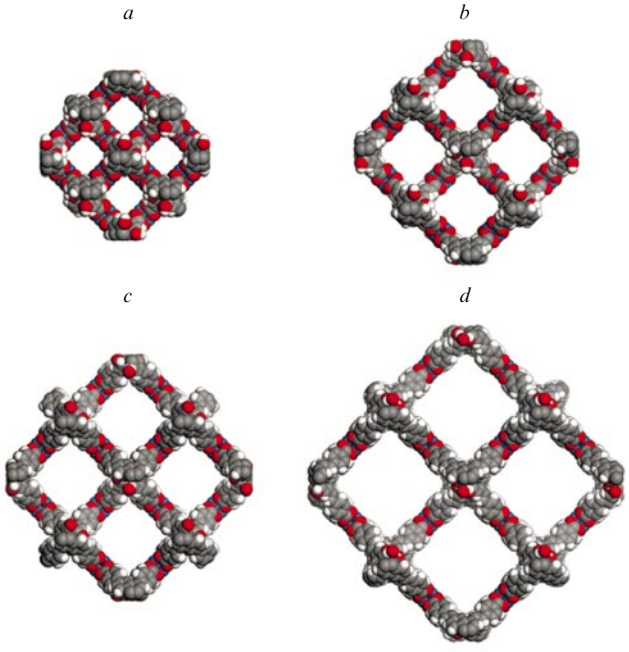
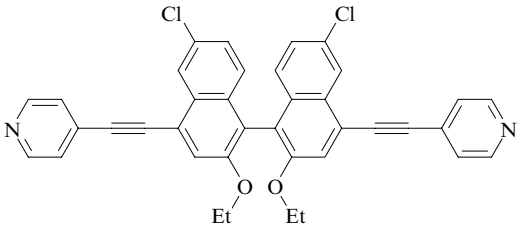


Figure 19. Comparison of the frameworks $[Cu_2((R)\text{-L})(solv)_2]$ of compounds **34** (*a*), **36** (*b*), **37** (*c*) and **38** (*d*).[52, 53]

A family of mesoporous isoreticular homochiral metal-organic coordination polymers **36**–**38** of the general formula $[Cu_2((R)\text{-L})(solv)_2]\cdot x\,G$, where L = (R)-$(L13)^{4-}$ (**36**), (R)-$(L14)^{4-}$ (**37**) and (R)-$(L15)^{4-}$ (**38**); (solv is solvent; and G denotes the guest DMF and/or water molecules) was reported.[53]

The frameworks of compounds **36**–**38** are isoreticular with respect to the framework of $[Cu_2((R)\text{-L12})(H_2O)_2]$ (see Fig. 19 *b*–*d*). The void space in these compounds reaches a value of 92%, a maximum cross section of the channel is 32 Å. However, unoccupied frameworks are unstable due to the large void space. Nevertheless, this void size allows guest DMF molecules to be exchanged with ease by other substrates.

Two homochiral porous MOFs, $[Cu_3(L16)_4(dmf)_6.(H_2O)_3(ClO_4)](ClO_4)_5\cdot 10\,DMF\cdot 10\,EtOH\cdot 7\,H_2O$ (**39**) and $[Cu_3(L16)_5(dmf)_8](ClO_4)_6\cdot 6\,DMF\cdot 8\,EtOH\cdot Et_2O\cdot 6\,H_2O$ (**40**), were synthesized using the binaphthyl ligand L16 containing pyridine rings.[54]



L16

The framework of compound **39** has a complex 3D structure comprised of interpenetrating layers (Fig. 20). Nevertheless, the guest-accessible volume is 52%. Compound **40** is formed from the same reactants at adifferent temperature and has a layered structure. The layers stack on top of each other, the interlayer separation is ~8 Å and the channel cross-section is 14 × 21 Å. The channels are filled with the guest solvent molecules, perchlorate anions and with the chain coordination polymer [CuL16]. The guest-accessible volume is 50% (taking account of the [CuL16] chains). The stability of this structure was not studied.

The ligand L17 obtained by coupling of 4′-(4-bromophenyl)-2,2′:6,2″-terpyridine with (*S*)-6-ethynyl-1,1′-binaphthyl-2,2′-diol followed by treatment with hexamethylphosphorus triamide,

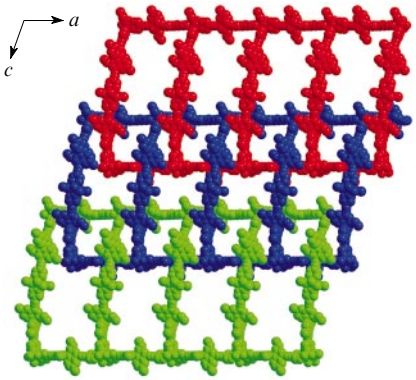
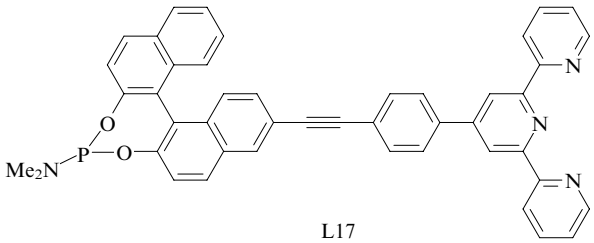


Figure 20. Interlocking of the networks $[Cu_3(L16)_4(dmf)_6(H_2O)_3.(ClO_4)]^{5+}$ of compound **39**.[54]



L17

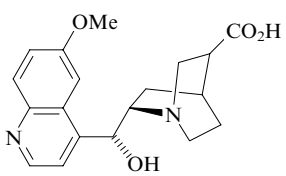
forms a violet amorphous precipitate insoluble in organic solvents upon the addition of iron(II) and rhodium(I) salts.[55] It was assumed that the heterometallic polymer thus obtained has a chain structure due to the fact that iron cations are coordinated to nitrogen atoms of two terpyridine fragments while the rhodium ion is coordinated to two phosphorus atoms. Despite the fact that the structure of this metal-organic coordination polymer is unknown, its interesting catalytic properties were revealed (see Section III).

Summing up, examples of using 1,1′-binaphthyl derivatives bearing functional substituents (carboxyl groups, phosphone groups, pyridine, *etc.*) for the synthesis of homochiral porous metal-organic coordination polymers have been well documented. Most of these compounds have stable frameworks, *i.e.*, they lose guest solvent molecules on heating but retain long-range order. The fraction of the void space in such compounds can be as high as 92%! However, the approach considered above does not always lead to porous products. For instance, the synthesis of homochiral nonporous metal-organic coordination polymers based on 1,1′-binaphthyl derivatives was reported.[37,56–63]

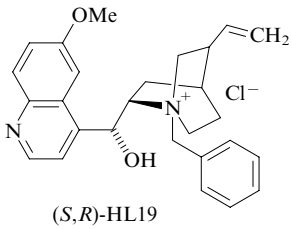
b. Coordination polymers based on quinine derivatives

A number of studies on the synthesis of homochiral metal-organic coordination polymers using quinine derivatives are available.[64–69] However, most compounds thus obtained are salts or have porous structures; therefore, nonlinear optical and/or ferroelectric properties of such compounds are mainly studied.

Mention may be made of a study[64] on the synthesis of compound **41** using quinine derivative HL18.



(*S*,*R*)-HL18



(*S*,*R*)-HL19

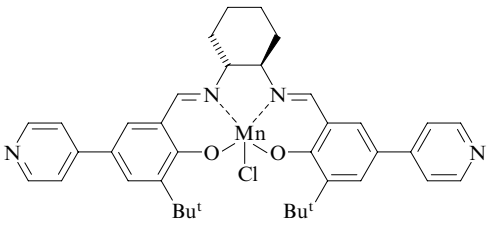
Under hydrothermal conditions, cadmium hydroxide and HL18 form a homochiral metal-organic coordination polymer $[Cd(L18)_2]$ (**41**). The structure of polymer **41** comprises a distorted diamond-like framework.

A layered metal-organic coordination polymer $[Cu_5Cl_6.(L19)_2]\cdot EtOH$ (**42**) was synthesized from the quinine salt HL19 and copper(I).[65] Compound **42** has a layered structure. The interlayer space is filled with ethanol molecules; however, no information on the framework stability after removal of the solvent molecules was reported.

c. Coordination polymers based on transition metal salen complexes

The synthesis of homochiral porous coordination polymers based on the derivatives of transition metal salen complexes is a promising research avenue because such complexes are catalysts of enantioselective transformations.[70–72] However, additional functionalization of the salen complexes to obtain polymeric structures faces significant synthetic difficulties.

One of the first syntheses[73] of a homochiral metal-organic coordination polymer carried out using a salen complex L20



(*R*,*R*)-L20

and biphenyl-4,4′-dicarboxylic acid (H_2bpdc) resulted in $[Zn_2(bpdc)_2(L20)]\cdot 10\,DMF\cdot 8\,H_2O$ (**43**). The structure of polymer **43** contains dinuclear fragments $\{Zn_2(COO)_4\}$ that bind to biphenyldicarboxylate anions, thus forming tetragonal networks. The layers are linked by salen N-donor ligands to form a framework (Fig. 21) comprising two interpenetrating networks and having rather large channels with cross-sections of 6×15.5 and 6×6 Å. When heated *in vacuo*, compound **43** loses long-range order, but its structure is restored upon adding DMF.

A large series of coordination polymers of first-row transition metals, magnesium and cadmium was synthesized using a bis(catechol) derivative of manganese(III) salen complex (L21).[74]

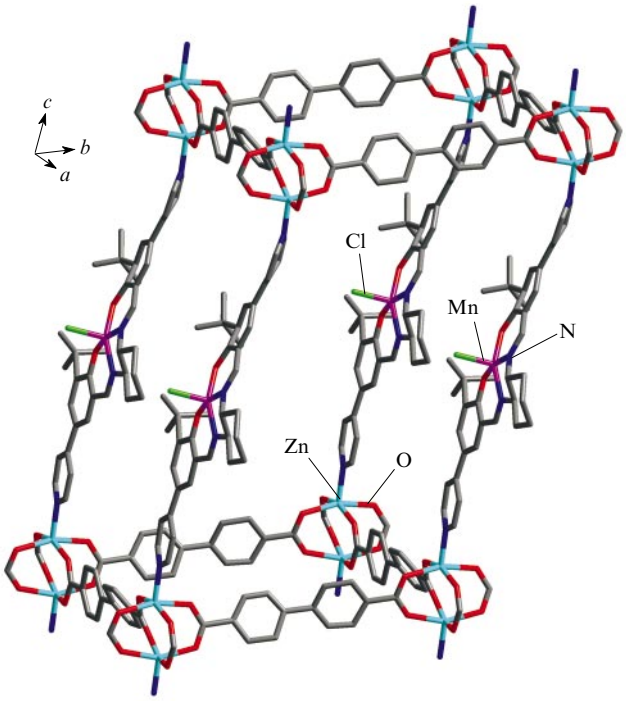
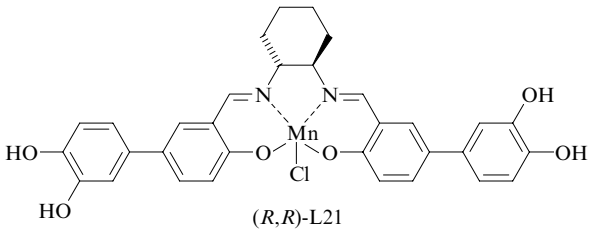


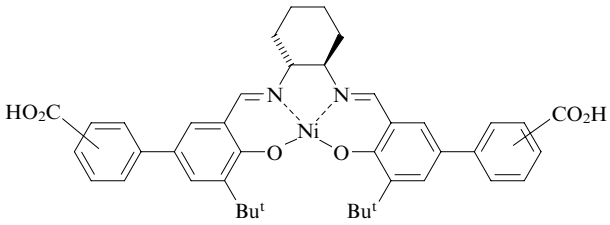
Figure 21. View of a single network unit $[Zn_2(bpdc)_2(L20)]$ of compound **43**.[73]



(*R*,*R*)-L21

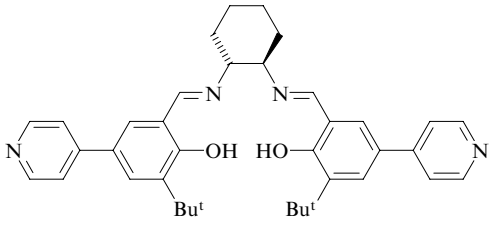
The ligand L21 is prone to form chain polymeric structures involvng chelating hydroxyl groups. None of the coordination polymers obtained from this ligand were characterized by X-ray difftaction. All compounds were tested for catalytic properties (see Section III).

Homochiral MOF based on salen complexes of nickel were reported.[75] Compounds **44** of the general formula $[Ni(L22)_2(L')_2]\cdot x\,G$ (L′ is pyridine or methanol, G stands for solvent molecules) have chain structures and catalyze stereospecific transformations.



(*R*,*R*)-H_2L22

Single crystals of $[Zn_6(L23)]\cdot 6\,THF$ (**45**) were obtained in high yield by heating zinc nitrate and *N*,*N*′-bis-[3-*tert*-butyl-5-(4-pyridyl)salicylidene]-1,2-diaminocyclohexane (H_2L23) in a DMF/THF/water mixture.[76]



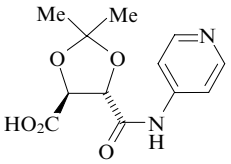
(*R*,*R*)-H_2L23

Structure **45** contains channels with a cross-section of 14×11 Å, filled with THF molecules. The framework is permanently porous; the internal surface area is 504 $m^2\,g^{-1}$.

Only a few examples of homochiral metal-organic coordination polymers based on selen complexes have been reported so far. This can be explained by complexity of the synthesis of these ligands. However, all of them are highly active in stereospecific catalysis and exhibit other interesting properties.[77–79]

d. Coordination polymers with other chiral ligands

Single crystals of compound $[H_3O]_2[Zn_3(\mu_3\text{-}O)(L24)_6]\cdot\cdot 12\,H_2O$ (**46**) were obtained by the reaction of zinc nitrate with a tartaric acid derivative HL24 in alcoholic aqueous solution.[80]



HL24

The structure of the metal-organic coordination polymer **46** conains trinuclear fragments $[Zn_3(\mu_3\text{-}O)(L24)_6]$ comprising three zinc cations coordinated to carboxyl groups of the ligand and to the μ_3-O atom. These trinuclear fragments form layers (Fig. 22) separated by a distance of 15.5 Å. The layers are arranged in such a fashion that hexagonal channels 13.5 Å in diameter are formed. The guest-accessible volume is 47%. A complete removal of guest molecules *in vacuo* causes the compound to lose long-range order, but treatment with water leads to restoration of the crystal structure.

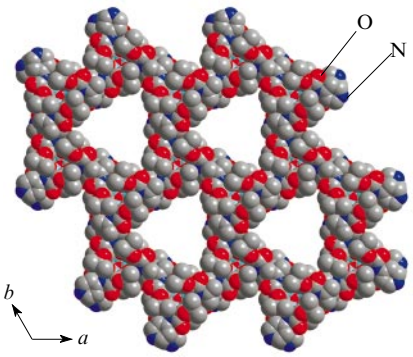
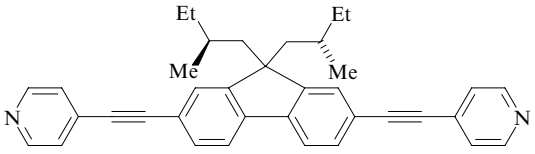


Figure 22. View of a network unit $[Zn_3(\mu_3\text{-}O)(L24)_6]^{2-}$ of compound **46**.[80]

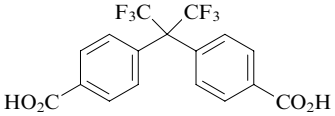
A solution of copper(II) nitrate in ethanol was slowly layered onto a solution of the ligand L25 {L25 is 9,9-bis[(*S*)-2-methylbutyl]-2,7-bis(4-pyridylethynyl)fluorene}



(*S*)-L25

in dichloromethane; crystals of $[Cu(L25)_2(NO_3)_2]\cdot 2\,EtOH$ (**47**) were obtained at the interface after two days.[81] This metal-organic coordination polymer has a layered structure with three-layer packing (Fig. 23). The structure contains channels with a cross-section of 8 × 8 Å; the guest-accessible volume is about 12%.

Yet another ligand is 4,4′-(hexafluoropropane-2,2-diyl)-bis(benzoic acid) (H_2L26).[82]



L26

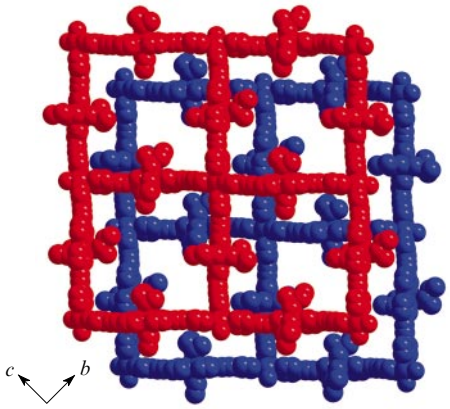
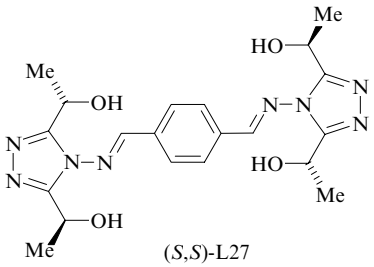


Figure 23. Stack of two square-grid layers $[Cu(L25)_2(NO_3)_2]$ of compound **47**.[81]

The structure of polymer [Zn(L26)] (**48**) contains a trinuclear zinc fragment. Compound **48** has a porous structure. Its framework contains two types of channels, namely, square channels with a cross-section of 8 × 8 Å and hexagonal channels 10 Å in diameter. The internal surface of the channels is 'decorated' with CF_3 groups. Compound **48** exhibits an unusually high thermal stability to 430 °C. Although ligand L26 is nonchiral, spontaneous resolution occurs during the reaction and same-chirality crystals are formed.

The structure of compound $[Ag_4(L27)_3(NO_3)_4]\cdot \cdot 10\,MeOH$ (**49**) has a unique topology and comprises three interpenetrating networks (Fig. 24).[83]



(*S*,*S*)-L27

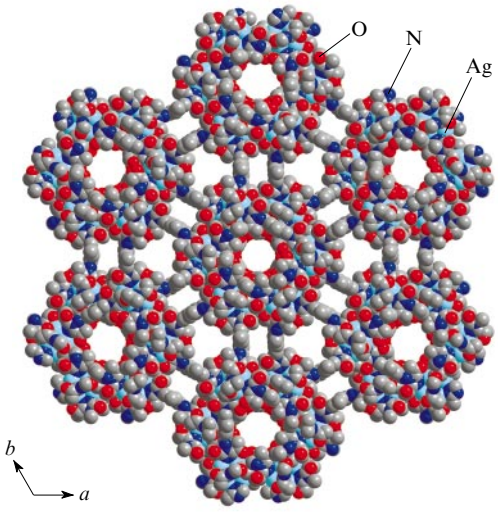
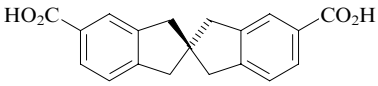


Figure 24. View of a layer fragment $[Ag_4(L27)_3(NO_3)_4]$ of compound **49**.[83]

The framework is penetrated by channels 8 Å in diameter. It should be noted that the internal surface of the channels is 'decorated' with OH groups and thus exhibits hydrophilic properties. The framework is stable to removal of guest solvent molecules (10 methanol molecules per formula unit); the polymer retains long-range order up to 125 °C. Compound **49** exhibits the sorption properties towards some aromatic compounds.

Reaction of (*S*)-2,2′-spirodiindane-5,5′-dicarboxylic acid (H_2L28) with zinc nitrate gives $[Zn_4O((S)\text{-L28})_3]\cdot 10\,DMF\cdot 3.5\,H_2O$ (**50**).[84]



(*S*)-H_2L28

This compound is built of Zn_4O units coordinated to carboxylate groups of the chiral ligand. Two interpenetrating frameworks form channels with a cross-section of 8 × 14 Å; the guest-accessible volume is 63%.

As can be seen, homochiral coordination polymers based on optically active organic ligands of different nature (binaphthyl and quinine derivatives, salen complexes, *etc.*) can have stable porous structures and exhibit the sorption properties to various substrates. A key problem in their synthesis consists in poor availability of optically pure, rigid polytopic bridging ligands.

2. The use of chiral template

Homochiral porous metal-organic coordination polymers are also synthesized from achiral reagents; here, chirality is induced by adding an optically active template. The enantiomerically pure template is not directly involved in the formation of the framework structure and acts as chirality inductor to suppress the formation of optical antipode (Fig. 25). We believe that the chiral template-based synthesis is a promising route to homochiral porous metal-organic coordination polymers. However, only a few studies on the subject have been reported so far.

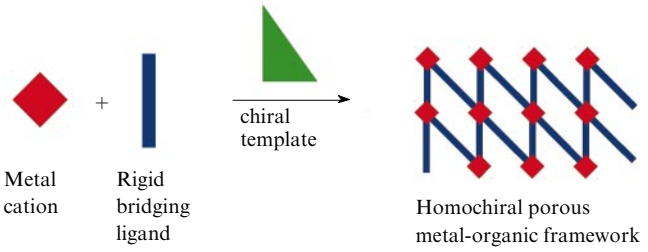


Figure 25. Synthesis using a chiral template: a scheme.

Homochiral porous metal-organic coordination polymers were synthesized based on propane-1,2-diol (1,2-Prd) and enantioselective sorption of substances on the synthesized compounds was studied.[85,86] Coordination polymers $[M_3(btc)_2(3\text{-pic})_6(1,2\text{-prd})_3]\cdot 9\,(1,2\text{-Prd})\cdot 11\,H_2O$ (**51**) and $[M_3(btc)_2(py)_6(1,2\text{-prd})_3]\cdot 9\,(1,2\text{-Prd})\cdot 11\,H_2O$ (**52**) (M = Co, Ni) are formed in the course of diffusion of 3-picoline (Pic) or pyridine vapours into a solution of corresponding metal nitrate and 1,3,5-benzene-tricarboxylic acid (H_3btc) in propane-1,2-diol. Using different optical isomers (*R* or *S*) of propane-1,2-diol, one can isolate the *R*- or *S*-form of the coordination polymers **51** and **52**. To test the optical purity of the entire phase, five X-ray experiments with randomly chosen single crystals were carried out. It appeared that they were of the same chirality. The framework structures of these compounds contain channels with a cross-section of 8.5 × 10.5 Å, as was proved by sorption experiments. The frameworks of the pyridine-based polymers **52** are destabilized upon removal of guest molecules and collapse, whereas the frameworks of the Pic-based compounds **51** retain crystallinity (the void space is ~47%).

3. The use of chiral polyfunctional ligands

When metal cations react with chiral polyfunctional ligands, the latter can simultaneously be coordinated to several cations, thus forming polynuclear metal complexes. Such complex polynuclear systems can act as secondary structural units and form metal-organic coordination polymers (Fig. 26). The main advantage of this approach is the possibility of using natural optically pure reagents, such as amino acids, hydroxy acids, polycarboxylic acids, *etc.* as ligands. Usually, they are readily available. However, nonrigidity and great coordination potential of these ligands make the polymer structure predictions almost impossible. In particular, this method gives no warranty that the final coordination polymer will be porous.

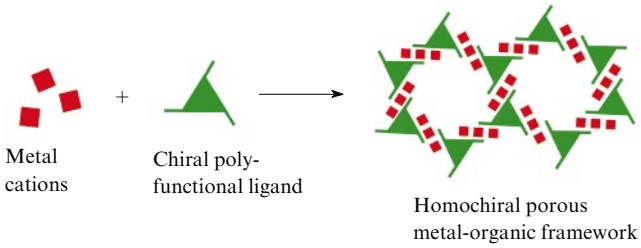
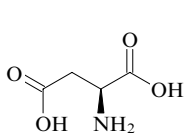


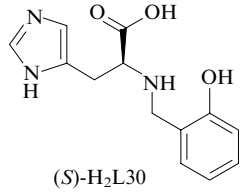
Figure 26. Synthesis using a chiral polyfunctional bridging ligand: a scheme.

a. Homochiral porous coordination polymers based on amino acids and their derivatives

Homochiral metal-organic coordination polymers were synthesized using (*S*)-aspartic acid.[87,88] Under hydrothermal conditions, the reaction of nickel chloride with (*S*)-aspartic acid [(*S*)-H_2L29] in the presence of different amounts of triethylamine results in $[Ni_2O((S)\text{-L29})(H_2O)_2]\cdot 2\,H_2O$ (**53**) or $[Ni_{2.5}(OH)((S)\text{-L29})_2]\cdot 6.55\,H_2O$ (**54**).



(*S*)-H_2L29



(*S*)-H_2L30

The structures of compounds **53** and **54** contain trinuclear nickel fragments $[Ni_3O_{10}N(H_2O)_3]$ that form chains. In compound **54**, these chains form a framework involving an octahedral complex $[Ni((S)\text{-L29})_2]^{2-}$ (Fig. 27). Evacuated samples exhibit sorption properties; however, the uptake is somewhat smaller than the calculated value.

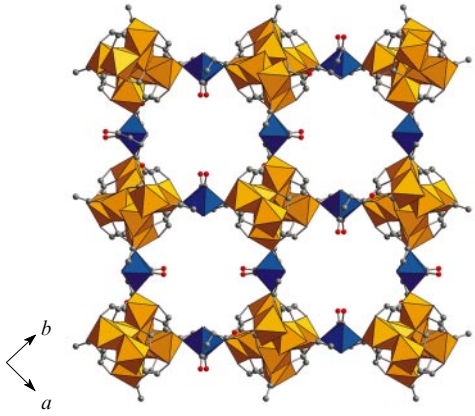
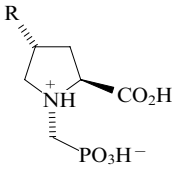


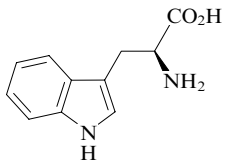
Figure 27. Structure of the framework $[Ni_{2.5}(OH)((S)\text{-}L29)_2]$ of compound **54**.[88]

This suggests partial collapse of the framework upon removal of guest molecules. Reactions using the ligand (*S*)-H_2L30 led to related complexes.

A number of homochiral porous metal-organic coordination polymers are based on lanthanides and (*S*)-*N*-phosphomethylproline (H_2L31) and have the general formula $[Ln(H_2L31)_3]\cdot 2\,H_2O$ (**55**), where Ln = Tb, Dy, Eu, Gd.



R = H [(*S*,*S*)-H_3L31],
HO [(*S*,*S*,*R*)-H_3L32].



(*S*)-HL33

Isostructural compounds **55** have framework structures (Fig. 28) and small guest-accessible volumes. The frameworks do not collapse upon complete removal of guest water molecules, as was confirmed by nitrogen sorption data.

Compounds H_2L31 and 4-hydroxy-*N*-phosphomethylproline (H_3L32) were used for the synthesis of metal-

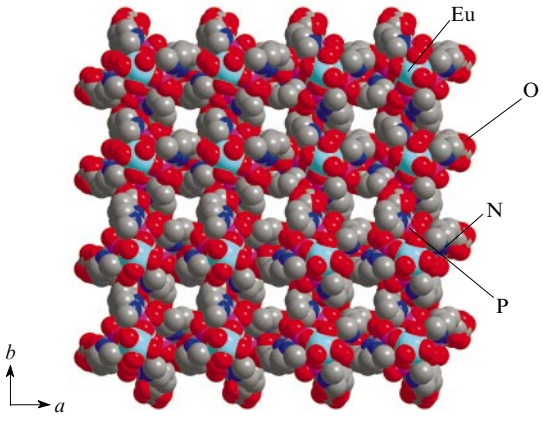


Figure 28. Structure of the framework $[Ln(H_2L31)_3]$ of compounds **55**.[89]

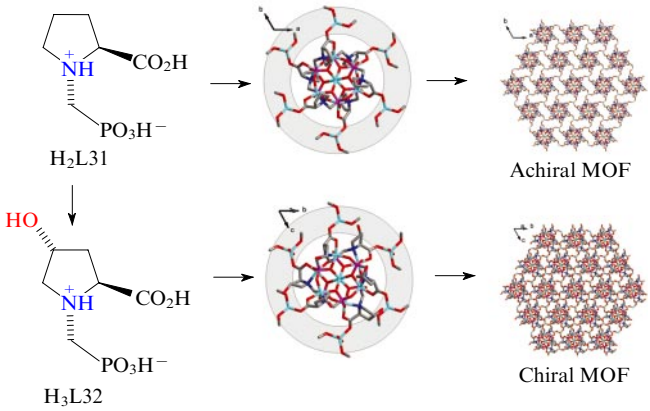
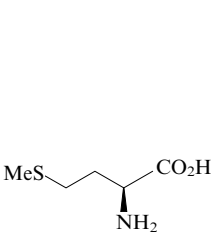


Figure 29. The synthesis of $[Zn_9(L31)_6(H_2O)_2]\cdot 13.5\,H_2O$ (**56**) and $[Zn_9(L32)_6(H_2O)_3]\cdot EtOH\cdot 8.5\,H_2O$ (**57**).[90]

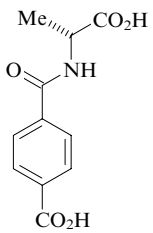
organic coordination polymers $[Zn_9(L31)_6(H_2O)_2]\cdot \cdot 13.5\,H_2O$ (**56**) and $[Zn_9(L32)_6(H_2O)_3]\cdot EtOH\cdot 8.5\,H_2O$ (**57**) (Fig. 29).[90] In structure **56**, the ligand L31 coordinates zinc cations to nitrogen and oxygen atoms. The structure of this compound comprises the $[Zn_7(L31)_6][Zn_6(H_2O)_6]$ units containing three types of zinc cations with different coordination numbers equal to 6, 5 and 4. Compound **56** is achiral, apparently, due to racemization of the ligand under the synthesis conditions. The metal-organic coordination polymer **57** was synthesized using the modified *N*-phosphomethylproline (H_3L32) to introduce additional chiral centres into the framework. Compound **57** crystallizes in the chiral space group and, generally, is structurally similar to **56**. Both structures contain channels with a cross-section of 4×5 Å.

The homochiral metal-organic coordination polymers based on (*S*)-tryptophan (HL33) include $[Co_2((S)\text{-}L33)_2(py)_6](ClO_4)_2\cdot Py$ (**58**) and $[Ni((S)\text{-}L33)(py)_3]ClO_4\cdot \cdot H_2O$ (**59**).[91] Both compounds have identical coordination environments of metal atoms and similar structures of the 'building blocks' and helical chains; however, the frameworks differ in packing of helices. The frameworks contain channels with cross-sections of 5×8 and 2×3 Å for **58** and 6×8 and 3×3 Å for **59**. The channels are occupied by pyridine and water molecules and by perchlorate anions.

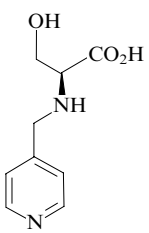
The synthesis, structure and stability of a methionine (HL34) based heterometallic homochiral porous metal-organic coordination polymer $[Ag_3Cu^{II}((S)\text{-}L34)_6(NO_3)_3\cdot .(H_2O)_3]\cdot 7\,H_2O$ (**60**) was reported.[92]



(*S*)-HL34



(*R*)-H_2L35



(*S*)-HL36

In this compound, methionine carboxyl groups are coordinated to the copper atom and sulfur atoms are coordinated to the silver atom. Structure **60** contains three crystallographically independent copper atoms, of which two have a trigonal-bipyramidal environment and the third

Cu atom is in octahedral environment. Silver cations have a tetrahedral coordination environment and form trimers linked by μ_2-S atoms. The coordination sphere of the silver ion is completed by water molecules. The copper atom forms with methionine helical chains linked by silver-containing units to form a framework with a channel porous structure (Fig. 30). The size of the channel cross-section is 12×22 Å. Voids are occupied by nitrate anions and water molecules that form a system of strong hydrogen bonds. Theoretically, it seems possible to remove water molecules coordinated to the silver atom under mild conditions to obtain catalytically active sites within the framework. However, thermal stability studies showed that compound **60** loses crystallinity at 50 °C (*cf.* 200 °C needed to remove all water molecules). It should be noted that re-hydration of amorphous samples leads to restoration of the crystal structure; this procedure can be repeated several times.[92]

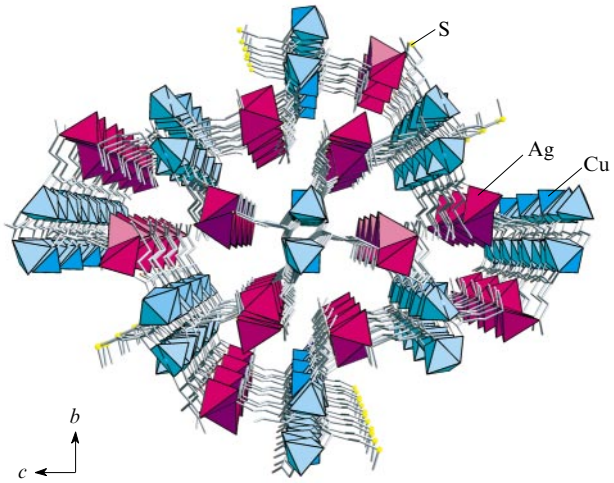


Figure 30. View of the framework $[Ag_3Cu_3((S)\text{-L34})_6(NO_3)_3 \cdot (H_2O)_3]$ of compound **60**.[92]

A derivative of alanine H_2L35 was used to synthesize zinc- and cadmium-based coordination polymers $[Zn_2(L35)_2(H_2O)_6]$ (**61**) and $[Cd_8(L35)_8(H_2O)_{20}] \cdot 15\,H_2O$ (**62**).[93] Compound **61** has a porous structure comprised of coordination chains linked by hydrogen bonds and $\pi-\pi$-interactions to form helices (Fig. 31). Structurally, compound **62** is composed of four interpenetrating frameworks built of double helices linked in such a manner that the final structure is porous and has the topology of a diamond.

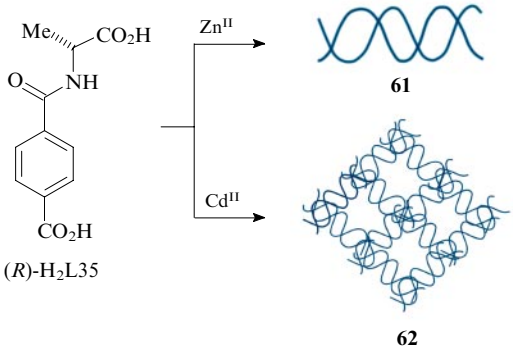


Figure 31. Synthesis and schematic representation of the structures $[Zn_2(L35)_2(H_2O)_6]$ (**61**) and $[Cd_8(L35)_8(H_2O)_{20}] \cdot 15\,H_2O$ (**62**).[93]

The metal-organic polymer $[Cu_2(L36)Cl_2] \cdot H_2O$ (**63**) based on a derivative of (*S*)-serine HL36 has a porous 3D structure comprised of chains (Fig. 32) with a channel cross-section of 5×3 Å. The framework is stable up to 190 °C, as was confirmed by X-ray powder diffraction data.[94] An important feature of compound **63** is that it exhibits catalytic properties in the 1,2-addition reaction involving α,β-unsaturated ketones (see Section III).

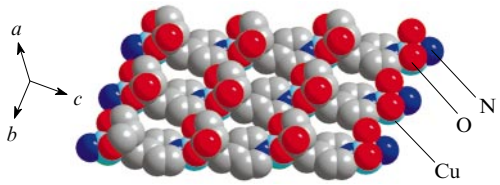
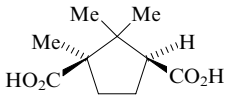


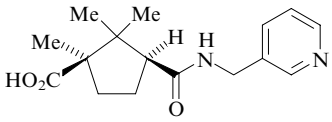
Figure 32. View of the framework $[Cu_2(L36)Cl_2]$ of compound **63**.[94]
The chlorine atoms are omitted.

b. Homochiral porous coordination polymers based on camphoric acid and its derivatives

A homochiral porous metal-organic coordination polymer based on magnesium and (*R*,*S*)-camphoric acid (H_2L37) has the formula $[Mg_2(HL37)_3(H_2O)_3](NO_3) \cdot MeCN$ (**64**) and a complex structure.[95]



(*R*,*S*)-H_2L37



(*R*,*S*)-HL38

The basic structural units for **64** are three-fold paddle wheels $[Mg_2(HL37)_3]$. For one magnesium cation, the remaining coordination sites are occupied by oxygens from carboxyl groups of camphoric acid; for the other cation, they are occupied by water molecules. This complex in the framework of $[Mg_{12}(HL37)_{12}(H_2O)_{12}]$ (Fig. 33) forms a distorted cube containing an encapsulated tetrahedron. Eight magnesium cations occupy vertices of the distorted cube with an edge length of 10 Å. Each cube contains a tetrahedron formed by the hydrated magnesium cations. Compound **64** loses crystallinity on heating *in vacuo*.

The synthesis and structure of two metal-organic coordination polymers based on uranyl cation and (*R*,*S*)-camphoric acid, $[UO_2(L37)_2(py)_2] \cdot Py$ (**65**) and $[UO_2(L37)_2 \cdot MeOH] \cdot MeOH$ (**66**), were reported.[96] In compound **65**, camphorate anion forms chiral chains with uranyl cation. Two oxygen and nitrogen atoms complete the coordination environment of uranium atom to a square antiprism. Chains are interlinked to form layers stabilized by van der Waals interactions. The interlayer space is filled with guest pyridine molecules. In structure **66**, uranyl cations form a dinuclear fragment linked by carboxyl groups of camphoric acid. The coordination environment of uranium atom is

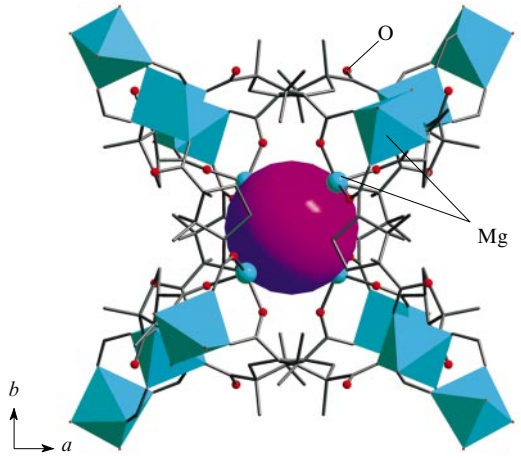


Figure 33. Fragment of the structure of compound **64**.[95]

completed by bridging oxygen atoms from carboxyl group of camphorate anion and by the oxygen atom of methanol. Thus, the coordination number of uranium in the second structure is 7. No stability and sorption studies of these compounds were carried out.

A study[97] on the synthesis, structure and nonlinear optical properties of metal-organic coordination polymers $[Cd(L38)_2(H_2O)]\cdot 5.5\,H_2O$ (**67**) and $[Cu(L38)_2(H_2O)]\cdot 4\,H_2O$ (**68**) based on the ligand L38 [(1*R*,3*S*)-1,2,2-trimethyl-3-(3-pyridylmethylcarbamoyl)cyclopentanecarboxylate] showed that both compounds have framework structures, the same topology and are built of chains linked by a network of hydrogen bonds (Fig. 34). Channels in these compounds are occupied by water molecules. In spite of the fact that the frameworks are stabilized by hydrogen bonds, they retain long-range order upon dehydration (both guest molecules and coordinated water molecules are removed).

Homochiral nonporous metal-organic coordination polymers based on camphoric acid are also known.[98–103]

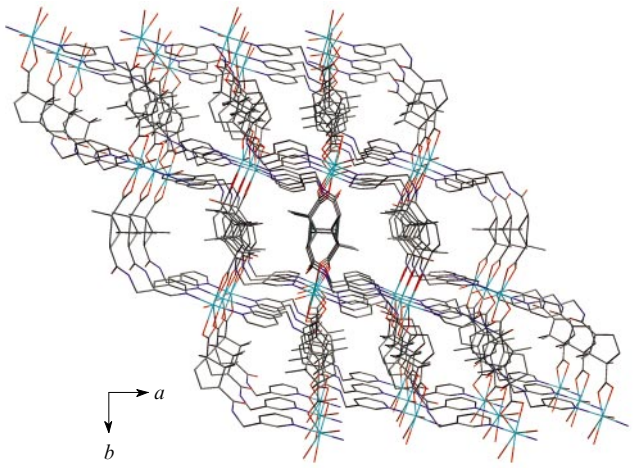
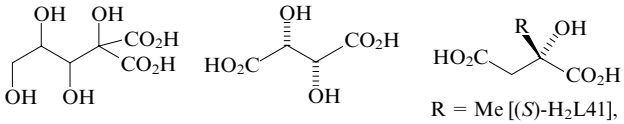


Figure 34. View of the framework $[Cd(L38)_2(H_2O)]$ of compound **67**.[97]

c. Homochiral porous coordination polymers based on other polyfunctional ligands

In 1987, Rose and co-workers[104] reported the synthesis and structure of a porous copper(II) compound $Na_2[Cu_9Cl_2.(L39)_6(H_2O)_3]\cdot x\,H_2O$ (**69**), where H_2L39 is 1,2,3,4-tetrahydroxybutane-1,1-dicarboxylic acid formed *in situ* in the oxidation of ascorbic acid.[104]



H_3L39 (*R*)-H_2L40 R = Me [(*S*)-H_2L41], H [(*S*)-H_2L42].

Compound **69** has a layered structure. The layers are held together through hydrogen bonds. The structure of metal-organic coordination polymer **69** contains channels about 20 Å in diameter filled with water molecules and sodium cations. The study cited[104] was published back in 1987 but has not yet attracted attention of researchers.

Porous lanthanide tartrates $[Ln_2((R)\text{-}L40)_3(H_2O)_2]\cdot\cdot 3\,H_2O$ (**70**), where Ln are lanthanides from La to Yb and Y, are isostructural to one another.[105] According to X-ray diffraction data, their structures contain three crystallographically independent tartrate anions. Two of them are chemically identical. They are coordinated to metal atoms through all six oxygen atoms. The third tartrate anion has an unusual coordination involving only carboxyl groups. The tartrate anions link the lanthanide cations to form open frameworks with hydrophilic channels with a cross-section of 5×7 Å. All lanthanide tartrates **70** retain crystallinity up to 250 °C, but undergo a number of phase transitions.

Replacement of the third type of tartrate anions by structurally similar succinate (suc) led[105] to yet another homochiral porous metal-organic coordination polymer $[Ln_2(R\text{-}L40)_2(suc)(H_2O)_2]\cdot 5.5\,H_2O$ (**71**). Compound **71** has the same topology and is isoreticular to the lanthanide tartrates **70** (Fig. 35). The channel cross-section in this framework is somewhat larger (6×9 Å). Compound **71** also shows high thermal stability.

Reactions of Zn^{2+} and Cu^{2+} salts with potassium tartrate and nitrogen-containing ligands 4,4′-bipyridine (bipy) and *trans*-1,2-bis(4-pyridyl)ethylene (bpe) afforded homochiral metal-organic coordination polymers $[Zn_2((R)\text{-}L40)_2(bipy)(H_2O)]\cdot 5.25\,H_2O$ (**72**), $[Cu((R)\text{-}L40)(bipy)]\cdot\cdot 2.33\,H_2O$ (**73**) and $[Cu((R)\text{-}L40)(bpe)]\cdot 8\,H_2O$ (**74**).[106] The volume accessible to guest water molecules is 31% (**72**), 18% (**73**) and 20% (**74**). An attempt to remove guest molecules without losing crystallinity succeeded only for compounds **72** and **73**.

A homochiral coordination polymer based on citramalic acid (H_2L41) $[Nd_7((S)\text{-}HL41)_8(NO_3)(H_2O)_8](CO_3)_2\cdot 4\,H_2O$ (**75**) has a complex 3D structure (Fig. 36).[107] Cylindrical channels 3.5 Å in diameter intercross in three dimensions, thus forming a complex system of channels. The total volume of channels is 22%.

Porous nickel and copper tartrates with the general formula $[M_2((R)\text{-}H_2L40)_2(H_2O)_2]\cdot 3\,H_2O$ (**76**) are isostructural.[108,109] Structure **76** contains dinuclear fragments $[M_2((R)\text{-}H_2L40)_2]$ (M = Cu, Ni). The framework represents a 3D network built of chiral nickel or copper tartrate layers linked by hydrogen bonds between water molecules in the

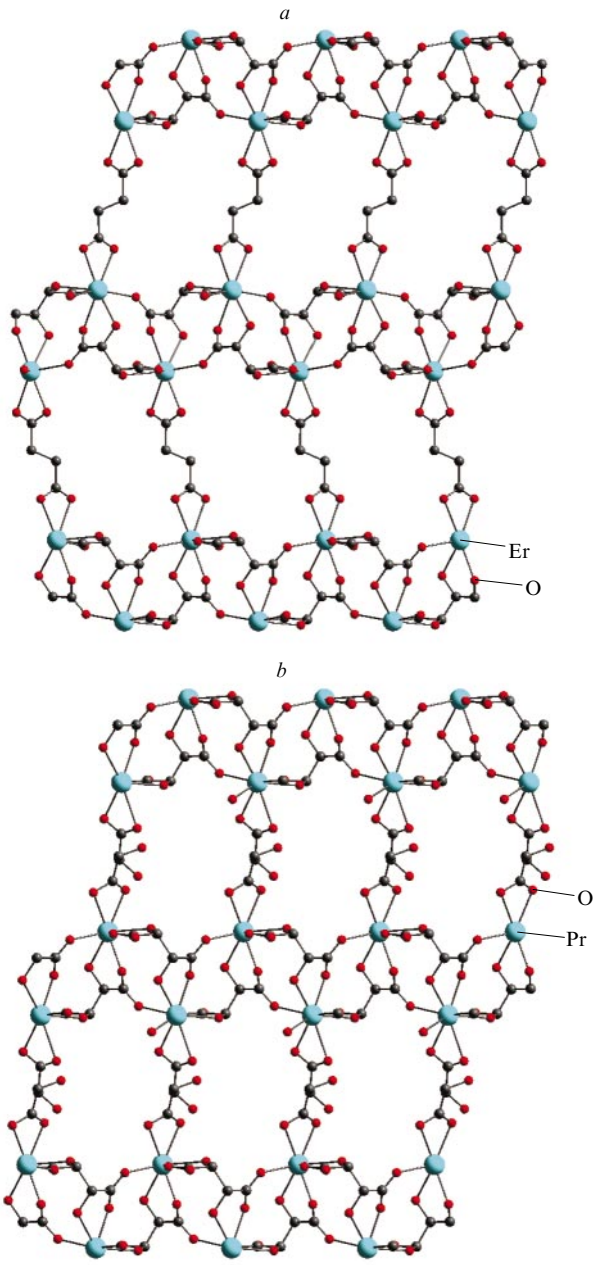


Figure 35. Comparison of two frameworks, $[Er_2((R)\text{-}L40)_3(H_2O)_2]$ of compound **70** (*a*) and $[Pr_2((R)\text{-}L40)_2(suc)(H_2O)_2]$ of compound **71** (*b*).[105]

interlayer space and uncoordinated oxygen atoms of carboxyl groups. Compounds **76** lose guest water molecules on heating to 150 °C. The crystal structure of nickel tartrate was studied as function of temperature. A phase transition in the temperature range from 85 to 100 °C was revealed. An X-ray diffraction study of the new phase revealed another type of the framework owing to the formation of four additional Ni—O bonds and its nonporous character.

A homochiral metal-organic coordination polymer based on malic acid (H_2L42) and magnesium, $[Mg((S)\text{-}L42)(H_2O)_2]\cdot H_2O$ (**77**), was reported.[110] Compound **77** has a 3D structure with helical motifs. Small channels are occupied by water molecules. No framework stability and sorption studies were reported.

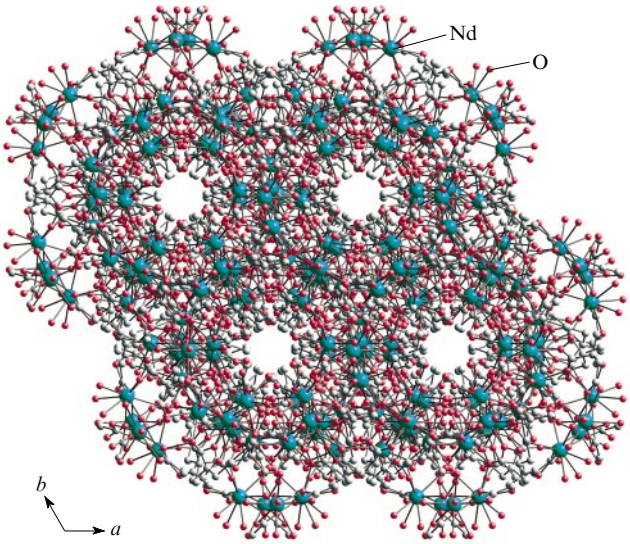


Figure 36. View of a fragment of the layer $[Nd_7((S)\text{-}HL41)_8.(NO_3)(H_2O)_8]$ of compound **77**.[110]

Summing up, the available literary sources provide information on the synthesis of homochiral porous metal-organic coordination polymers using chiral polyfunctional ligands, such as amino acids and their derivatives, camphoric and other polycarboxylic acids. However, the number of porous metal-organic coordination polymers is considerably smaller than that of nonporous compounds based on these ligands.[111–119]

4. Post-synthetic modification

Post-synthetic modification of achiral porous metal-organic coordination polymers with chiral ligands is an alternative to the synthesis of homochiral porous coordination polymers (Fig. 37). Successful modification of a metal-organic coordination polymer for catalytic or sorption applications requires that the initial compound should exhibit certain properties. First, it should be thermally and chemically stable. Second, its internal surface should have some sites suitable for further modification, *e.g.*, coordinatively unsaturated metal centres or functional groups. Based on the stable metal-organic framework, one can even vary chiral ligands (substituents), thus 'tuning' the properties of the final homochiral coordination polymer for various catalytic applications.

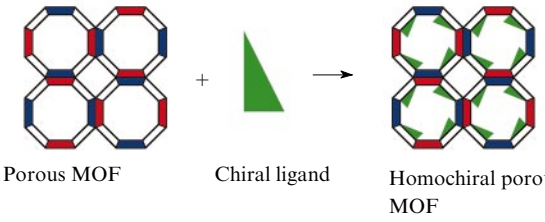
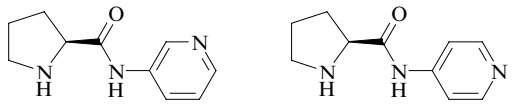


Figure 37. Synthesis by immobilization of optically pure ligand on the internal surface of the framework.

As far as we know, only one study carried out using this approach was reported to the time of writing this review.

Nevertheless, we believe that post-synthetic modification of stable porous metal-organic coordination polymers is a promising method of targeted synthesis of homochiral compounds.

Researchers from the group headed by Kim [120] used well known, thermally and chemically stable mesoporous chromium carboxylates $[Cr_3O(H_2O)_2X(bdc)_3]\cdot 25\,H_2O$ [H_2bdc is benzene-1,4-dicarboxylic (terephthalic) acid; $X = F^-$, HO^-, NO_3^-] as metal-organic coordination polymers.[27] This metal-organic framework is commercially available as MIL-101. It has an extremely large internal surface area and mesopores of different size (12–14 and 29–34 Å). Coordinatively unsaturated metal centres in the framework can be generated by heating MIL-101. The modifiers were proline derivatives, namely, (*S*)-*N*-(3-pyridyl)pyrrolidine-2-carboxamide (L43) and its 4-isomer L44, because proline and its derivatives are efficient catalysts of enantiospecific organic reactions.[121, 122]



(*S*)-L43 (*S*)-L44

The modified homochiral porous metal-organic frameworks MIL-101 with the ligands L43 and L44 were characterized by a number of physicochemical methods that confirm the inclusion of proline derivatives (1.8 molecules per formula unit) and continuity of the initial framework, although chemical bonding between the chiral molecules and the MIL-101 framework was not rigorously proved. The compounds obtained were studied as catalysts of asymmetric aldol condensation (see Section III).

5. Combining a chiral ligand and an achiral bridging ligand

This approach proposed in our study [123] involves a combination of two ligands, a chiral ligand and a rigid achiral bridging ligand, for the synthesis of homochiral metal-organic coordination polymers. The achiral ligand plays the role of a spacer and links chiral structural units into a porous framework (Fig. 38). The advantages of this method are as follows. First, a great potential for the design of homochiral porous metal-organic coordination polymers (in particular, it allows one to synthesize series of isoreticular homochiral porous metal-organic coordination polymers by varying the length of the bridging ligand). Second, one can use readily available natural chiral compounds, such as amino, hydroxy and polycarboxylic acids. Third, rigid polytope bridging ligands make the formation of porous structures more probable.

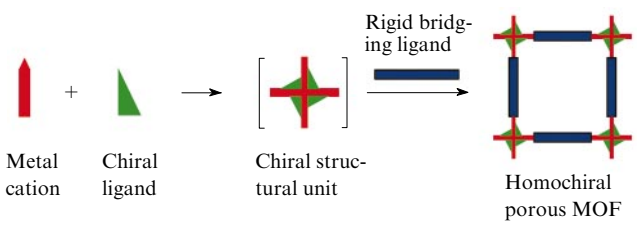


Figure 38. Synthesis using a combination of a chiral ligand and a rigid bridging ligand.

a. Coordination polymers synthesized using amino acids or their derivatives combined with various bridging ligands

A family of porous nickel(II), cobalt(II) and copper(II) aspartates including $[Ni_2((S)\text{-L29})_2(bipy)]\cdot MeOH\cdot H_2O$ (**78**), $[Cu_2((S)\text{-L29})_2(bpe)]\cdot x\,G$ (**79**), $[Ni_2((S)\text{-L29})_2(azpy)]\cdot\cdot(Azpy)_{0.6}\cdot(H_2O)_{1.4}$ (**80**), $[Ni_2((S)\text{-L29})_2(bpe)]\cdot x\,G$ (**81**), $[Ni_2((S)\text{-L29})_2(bpp)]\cdot 35\,(Bpp)_{0.33}\cdot(H_2O)_{1.333}$ (**82**) and $[Ni_2((S)\text{-L29})_2(py_3T)]\cdot x\,G$ (**83**) [azpy is 4,4′-azobipyridyl; bpp is 1,3-bis(4-pyridyl)propane; py_3T is 2,4,6-tris(4-pyridyl)triazine; G stands for guest solvent molecules] was reported.[124–128] Compounds **78**–**83** are structurally similar and composed of chiral metal aspartate layers (Fig. 39) that play the role of secondary structural units and are linked by various N-donor bridging ligands to form 3D networks. High thermal stability of the nickel- and cobalt-based frameworks is noteworthy. Stereoselective sorption and catalysis on the nickel metal-organic coordination polymers **78** and **81**–**83** was studied (see Section III).

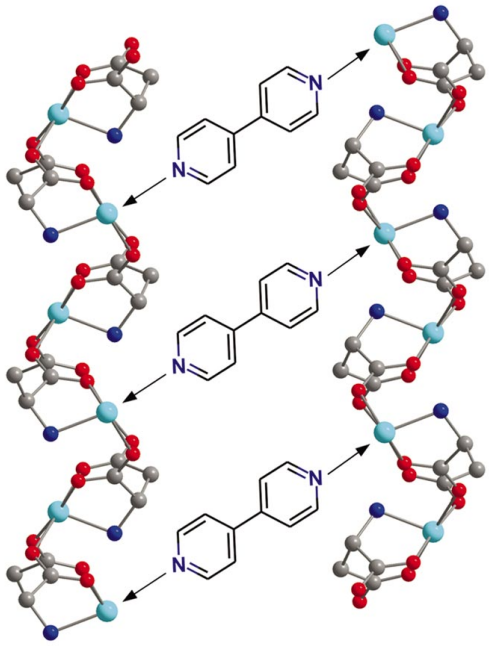
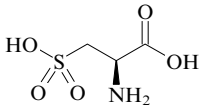


Figure 39. Mutual arrangement of the bipyridine bridging ligand and nickel aspartate in compound **78**.

Optically pure (*R*)-2-amino-3-sulfopropanoic acid (H_2L45)



(*R*)-H_2L45

and 4,4′-bipyridine were used to synthesize two metal-organic coordination polymers $[Co_2(L45)_2(bipy)_2(H_2O)_2]\cdot\cdot 3\,H_2O$ (**84**) and $[Co_2((R)\text{-L45})_2(bipy)(H_2O)_4]\cdot Bipy\cdot H_2O$ (**85**).[129] Compound **84** was obtained in a solvothermal reaction in a water/methanol mixture at 100 °C and polymer **85** was obtained by slow concentration of the water/methanol solution. Under the synthesis conditions of compound **84**, racemization of the chiral ligand occurs and the metal-organic coordination polymer has a 3D structure

composed of five interpenetrating helices; the cross-section of channels is 11×11 Å. On the contrary, compound **85** crystallizes in the chiral space group *P*1 and is built of layers linked by bipyridine bridging ligands (Fig. 40). This compound shows high thermal stability and retains crystallinity on heating to 245 °C.

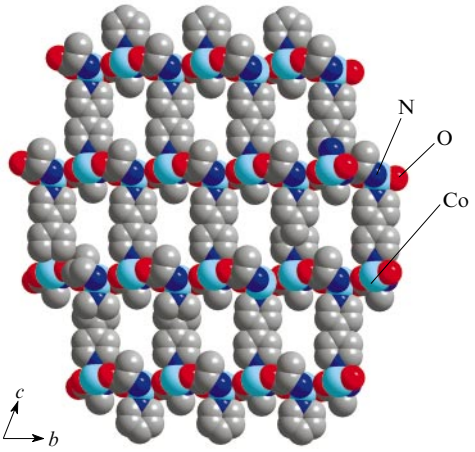


Figure 40. View of the framework $[Co_2((R)\text{-L45})_2(bipy)(H_2O)_4]$ of compound **85**.[129]

Thus, coordination polymers based on amino acid derivatives and different linkers are of considerable interest owing to the availability of ligands. Some of them are characterized by high thermal stability and exhibit the sorption and catalytic properties in asymmetric processes (see Section III). However, a large number of nonporous compounds was also obtained using this approach.[92, 130–134] Yet another significant drawback of amino acids as chiral ligands is the tendency to racemization under the conditions of high-temperature synthesis in the presence of certain metals.[124, 127]

b. Coordination polymers based on camphoric acid and various bridging ligands

Camphoric acid (H_2L37) is a rigid chiral ligand; however, nonporous structures are mainly formed owing to small length of the camphorate bridge. Nevertheless, chains and layers of chiral metal camphorates can be considered as promising secondary structural units for the design of porous frameworks.

Isoreticular, homochiral porous camphorates of the general formula $[M_2(L37)_2L]\cdot x\,G$ (**86**), where M = Zn^{2+}, Cu^{2+}, Co^{2+}; L = 1,4-diazabicyclo[2.2.2]-octane (dabco), bipy, bpe; G = DMF and H_2O synthesized for the first time by varying the metals and bridging ligands are structurally similar and have different pore sizes.[135–137] They were characterized by various physicochemical methods including single-crystal X-ray diffraction. According to X-ray single crystal and powder diffraction data, compounds **86** contain a 'paddle-wheel'-type dinuclear tetracarboxylate fragments $[M_2(CO_2R)_4]$ that form chiral layers linked by camphorate bridges. This structural motif is common to the whole family of isoreticular camphorates. The layers are linked by N-donor ligands to form a framework with a cubic topology. The frameworks contain channels with cross-sections of 3×4, 5×7 and 5×10 Å for L = dabco, bipy and bpe, respectively (Fig. 41).

The thermal stability of metal-organic coordination polymers and as well as their stability to replacement of 'guest' molecules were studied. Copper camphorates lose crystallinity upon removal of guest solvent molecules on heating or upon their replacement by methylene chloride. Zinc camphorates $[Zn_2(L37)_2(dabco)]$ and $[Zn_2(L37)_2(bipy)]$ have permanently porous structures; this was confirmed by nitrogen sorption experiments (specific surface area is 553 and 1014 $m^2\ g^{-1}$, respectively). Camphorates **86** (M = Co) are stable to removal of guest molecules. The available results[135–137] suggest that metal camphorates **86** with long N-donor bridging ligand bpe are least stable, most probably, due to high fraction of the void space in the framework, which leads to the loss of crystallinity upon removal or replacement of the guest solvent molecules. Usually, in such cases the porous metal-organic coordination polymers are stabilized through interpenetration of frameworks, but close packing of atoms in the metal camphorate layers makes interpenetration impossible in the case of bpe ligand. The stability of porous zinc(II) camphorates to removal of guest molecules was studied by thermal kinetics methods.[138]

Compound $[Zn_2(L37)_2(apyr)]\cdot 2\,DMF$ (**87**) was obtained by heating stoichiometric amounts of zinc nitrate, racemic camphoric acid and 2-aminopyrazine (apyr) in DMF.[139] The chiral metal-organic coordination polymer **87** is structurally similar to zinc camphorates **86** and stable upon removal of guest DMF molecules; however, sorption of racemic alcohols revealed no enantiomeric selectivity.

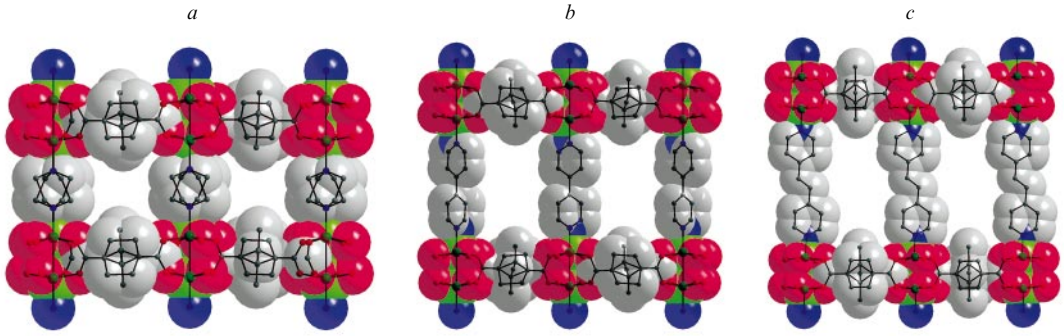
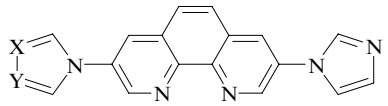


Figure 41. Comparison of isoreticular frameworks based on zinc camphorates $[Zn_2(L37)_2L]$ (**86**) for L = dabco (*a*), bipy (*b*) and bpe (*c*).[135–137]

Porous cadmium camphorate $[Cd(L37)(bpp)]\cdot 2\,H_2O$ (**88**) and cobalt camphorate $[Co(L37)(bpp)]\cdot 2\,H_2O$ (**89**) were synthesized.[140, 141] Compound **88** is built of cadmium camphorate chains linked by bpp ligands to form a framework structure. Owing to flexibility of the bridging ligand, heating of the metal-organic coordination polymer **88** causes a series of phase transitions resulting in nonporous phases α-[Cd(L37)(bpp)] (100 °C) and β-[Cd(L37)(bpp)] (140 °C); at 160 °C, the polymer loses crystallinity. Compound **89** has a more complex structure; its framework is composed of three interpenetrating networks. The properties of compounds **88** and **89** were not studied.

Metal-organic coordination polymers were synthesized[142] using camphoric acid and a long-chain bridging ligand 3,8-bis(imidazolyl)-1,10-phenanthroline which can exist as two conformers L46 and L47.



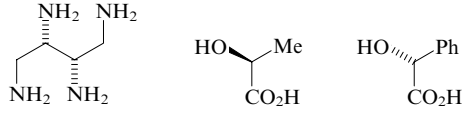
X = N, Y = CH (L46); X = CH, Y = N (L47).

Three compounds were obtained, *viz*., $[Cd_2(L37)_2\cdot(L46)_2]\cdot 6\,H_2O$ (**90**), $[Cd(L37)_2(L46)(H_2O)]$ (**91**) and $[Zn_2(L37)_2(L47)_2]\cdot 5\,H_2O$ (**92**). In structures **90** and **91**, the L46 conformer of the bridging ligand is involved in both chelate and bridging type coordination through the phenanthroline and imidazole nitrogen atoms, respectively. In structure **92**, the L47 ligand is coordinated to imidazole nitrogen atoms only by the bridging type. Compound **90** contains coordination chains linked by bridging camphorates into 2D networks. The interlayer space is occupied by water molecules responsible for strong layer-to-layer bonding through hydrogen bonds. Porous compound **91** has a complex 3D structure. The structure of polymer **92** is composed of zinc camphorate chains linked by N-donor bridging ligands to form a framework. The luminescence properties of all compounds were studied.

In addition, a number of studies on the use of camphoric acid in combination with various bridging ligands for the synthesis of homochiral metal-organic coordination polymers were published; however, the compounds obtained appeared to be nonporous.[110, 140, 143–148]

c. Coordination polymers synthesized using combinations of other chiral and bridging ligands

Two types of rhenium cluster complexes were for the first time used[149] as rigid bridging ligands. These are octahedral $[Re_6E_8(CN)_6]^{4-}$ (E = Te, Se, S) and tetrahedral $[Re_4Te_4\cdot(CN)_{12}]^{4-}$. The chiral ligand was (*S,S*)-1,2,3,4-tetraaminobutane (L48).



L48 (*S*)-H_2L49 (*R*)-H_2L50

The following compounds were isolated by crystallization from aqueous solutions and characterized by X-ray diffraction: $[Cu((S,S)\text{-L48})]_2[Re_4Te_4(CN)_{12}]\cdot 6.5\,H_2O$ (**93**), $[Cu((S,S)\text{-L48})]_2[Re_6Te_8(CN)_6]\cdot 13.5\,H_2O$ (**94**), $[Cu_2((S,S)\text{-L48})_3(NH_3)][Re_6Se_8(CN)_6]\cdot 2\,H_2O$ (**95**), $[Cu_2((S,S)\text{-L48})_3]\cdot[Re_6S_8(CN)_6]\cdot 3\,H_2O$ (**96**), $[Cu_2((S,S)\text{-L48})_2(NH_3)][Re_4Te_4\cdot(CN)_{12}]\cdot 4\,H_2O$ (**97**) and $[Cu((S,S)\text{-L48})(NH_3)]_2[Re_4S_{3.4}\cdot Te_{0.6}(CN)_{12}]\cdot 1.25\,H_2O$ (**98**). In these polymers, chiral chains [Cu((*S,S*)-L48)] are interlinked by the rhenium cluster complexes to form 2D networks (Fig. 42). It was shown that metal-organic coordination polymers **93** and **94** can reversibly exchange guest molecules.

Studies[123, 150, 151] are devoted to the development of synthetic procedures and to the synthesis of a unique family

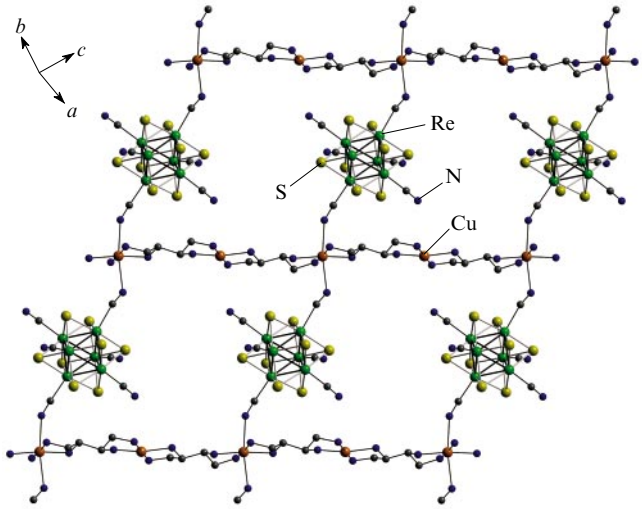


Figure 42. Structure of the framework $[Cu_2((S,S)\text{-L48})_3(NH_3)]\cdot[Re_6Se_8(CN)_6]$ of compound **95**.[149]

of isoreticular homochiral porous metal-organic coordination polymers of zinc based on (*S*)-lactic (H_2L49) and (*R*)-mandelic (H_2L50) acids.

The following metal-organic coordination polymers were obtained using different-length dicarboxylates as bridging ligands: $[Zn_2(bdc)((S)\text{-L49})(dmf)]\cdot DMF$ (**99**), $[Zn_2(ndc)((R)\text{-L50})(dmf)]\cdot 3\,DMF\cdot 0.5\,H_2O$ (**100**) and $[Zn_2\cdot(bpdc)((R)\text{-L50})(dmf)]\cdot 2\,DMF$ (**101**) (H_2ndc is naphthalene-2,6-dicarboxylic acid, H_2bpdc is biphenyl-4,4′-dicarboxylic acid). Compounds **99**–**101** were characterized by various physicochemical methods including X-ray diffraction. It was shown that in this series of compounds the guest-accessible volume increases from 40% to 60%, the pore cross-sections also increase, but all compounds share the same framework topology. According to X-ray diffraction data, zinc cations in compounds **99**–**101** have a coordination number of 5 and are linked into chiral chains by lactic or mandelic acid residues. The chains represent secondary 'building blocks' connected by bridging dicarboxylate ligands of different length in such a fashion that channels with a rhombic cross-section are formed (Fig. 43) to assemble a framework. The three compounds share the same topology, but have different channel cross-sections of 5×7 (**99**), 6×10 (**100**) and 4×14 Å (**101**). The polymers are also characterized by different environment and configurations of chiral centres. Stereoselective sorption involving compounds **99**–**101** and catalysis of the oxidation of organic sulfides were studied (see Section III).

Enantiomers $[Ag_2((S)\text{-L50})(bpp)_2]\cdot((S)\text{-}H_2L50)\cdot 3\,H_2O$ (**102**) and $[Ag_2((R)\text{-L50})(bpp)_2]\cdot((R)\text{-}H_2L50)\cdot 3\,H_2O$ (**103**) were synthesized[152] using mandelic acid as chiral ligand

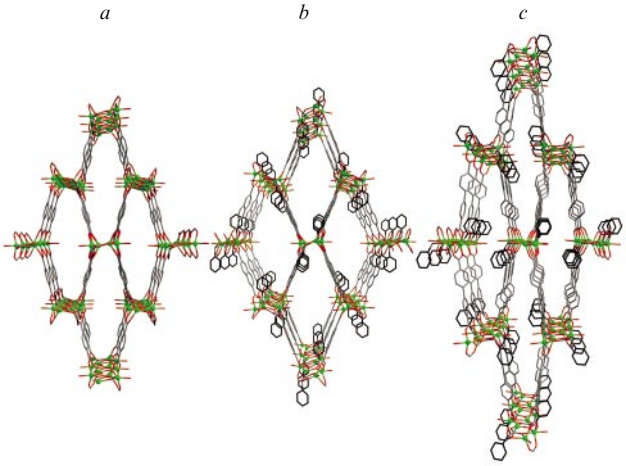
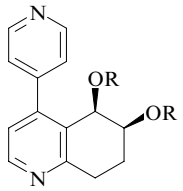


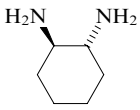
Figure 43. Comparison of the metal-organic frameworks $[Zn_2(bdc)((S)\text{-L49})(dmf)]$ (*a*), $[Zn_2(ndc)((R)\text{-L50})(dmf)]$ (*b*) and $[Zn_2(bpdc)((R)\text{-L50})(dmf)]$ (*c*).[123, 150, 151]

and 1,3-bis(4-pyridyl)propane as bridging ligand. Compounds **102** and **103** crystallize in enantiomorphic groups and have layered structures built of [Ag(bpp)] chains linked by the carboxyl group of mandelic acid. The inter-layer space is occupied by guest mandelic acid and water molecules which form layers stacked through hydrogen bonds. It should be noted that the use of racemic mandelic acid leads to some other compound whose structure is very sensitive to the solvent nature and varies with ease upon treatment with methanol or water vapours.

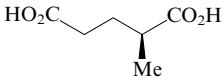
Two homochiral porous metal-organic coordination polymers based on fumaric acid (H_2fum) and bipyridyl derivatives L51 and L52 were reported.[153]



R = H ((*R*,*S*)-L51),
Me ((*R*,*S*)-L52).



L53



(*S*)-H_2L54

Their structures contain dinuclear zinc fumarate fragments $[Zn_2(fum)_4]$ that form layers. The layers are interlinked by the ligands L51 or L52 to form the $[Zn_2(fum)_2(L51)]$ or $[Zn_2(fum)_2(L52)]$ frameworks (Fig. 44).

Malic acid or a mixture of malic and succinic acids were used as chiral ligands while 4,4′-bipyridine was used to obtain porous structures.[154] Homochiral porous metal-organic frameworks $[Mn_2((S)\text{-L42})_{0.4}(suc)_{1.6}(bipy)_2 \cdot (H_2O)_2] \cdot Bipy$ (**104**) and $[Mn((S)\text{-L42})(bipy)(H_2O)] \cdot 3\,H_2O$ (**105**) have the same chemical compositions but different topologies. In compound **104**, one manganese coordination site is occupied by succinate anion while the other is 40% occupied by malate anion and 60% occupied by the succinate anion. The succinate and malate anions play the role of bridging ligands and link manganese cations to form 2D networks that are connected by 4,4′-bipyridine

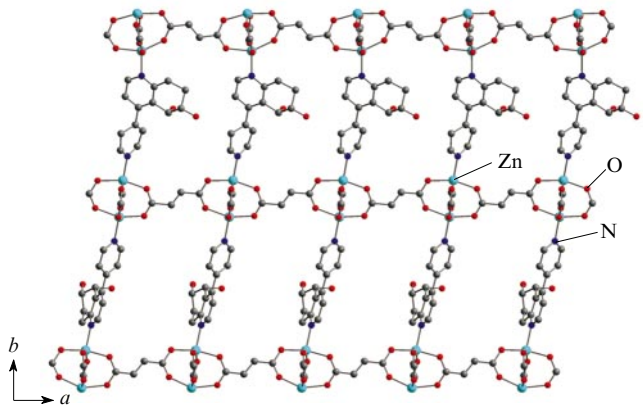


Figure 44. Structure of $[Zn_2(fum)_2(L51)]$.[153]

ligands to form a framework. Voids thus formed are occupied by 4,4′-bipyridine guest molecules. In polymer **105**, the malate anion acts as a μ_2-bridge and connects manganese cations into chains assembled to layers using 4,4′-bipyridine bridges. The layers form a framework stabilized by hydrogen bonds between uncoordinated carboxyl groups of malic acid and guest water molecules (Fig. 45). Channels in the framework have a cross-section of 9×11.5 Å. The guest-accessible volume is 35%.

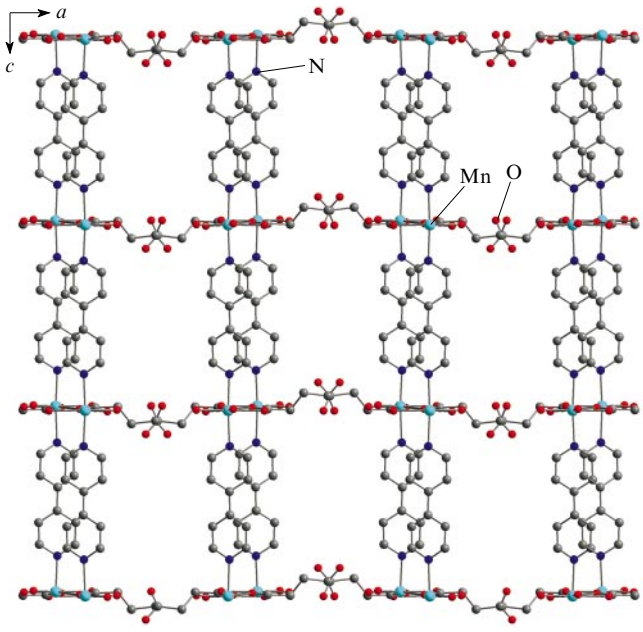


Figure 45. View of the framework $[Mn((S)\text{-HL42})(bipy)(H_2O)]$ of compound **105**.[154]

Two homochiral metal-organic coordination polymers based on optically pure (*R*,*R*)-1,2-diaminocyclohexane [(*R*,*R*)-L53] and bridging hexacyanoruthenate, namely, $[Cu((R,R)\text{-L53})_2]_2[Ru(CN)_6] \cdot 6\,H_2O$ (**106**) and $[Cu((R,R)\text{-L53})_2]_{12}[Ru(CN)_6]_6 \cdot 26\,H_2O$ (**107**), were synthesized.[155] Both compounds have 3D diamond-like structures with

voids occupied by water molecules. The guest-accessible volume is 25% (**106**) and 11.5% (**107**). The frameworks are stable to 140 °C.

Ferey and co-workers [156] reported the synthesis of compound $[Co_{20}((S)\text{-L54})_{12}(3\text{-mg})_8(H_2O)_8]\cdot 20\,H_2O$ (**108**) with a helical framework structure. Chiral 2-methyl glutarate [(*S*)-L54] was used as chirality inductor responsible for the handedness of the helices. Achiral 3-methyl glutarate (3-mg) plays the role of a bridging ligand and links chiral fragments to form a framework. Interestingly, the introduction of only chiral glutarate into the reaction with nickel salts leads to racemization of the glutarate and formation of compound $[Ni_{20}((R)\text{-L54})_{12}((S)\text{-L54})_8(H_2O)_8]\cdot 20\,H_2O$ (**109**). No solid products are formed in the case of cobalt salts. This was explained by the fact that nickel can catalyze racemization of amino acids, whereas cobalt can not. The homochiral framework of compound **108** has a guest-accessible volume of 10% and is stable on heating to 150 °C.

The examples presented in this Section show that the use of additional rigid spacer makes the formation of a porous product more probable. Most chiral ligands used in this approach are readily available in optically pure form. Coordination polymers thus obtained often have stable, permanently porous frameworks and some of them exhibit sorption and catalytic properties towards various substrates and reactions. In addition, an important and promising research avenue is the synthesis of series of isoreticular, homochiral, porous metal-organic coordination polymers with variable void geometries. Such metal-organic coordination polymers are also of interest for enantioselective resolution and catalysis.

III. Prospects for application

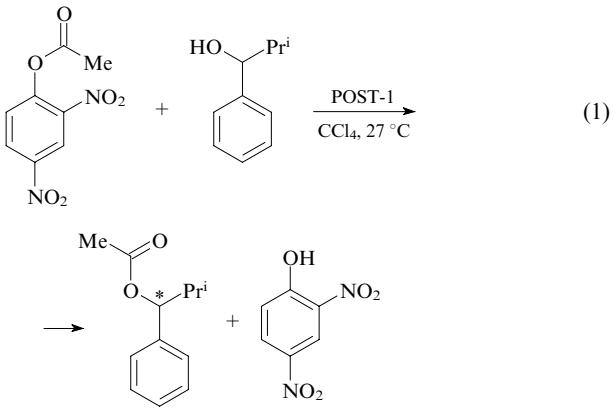
Homochiral porous metal-organic coordination polymers are promising for wide use in enantioselective processes, first of all, catalysis and sorption. As to nonporous metal-organic coordination polymers with chiral structures, their nonlinear optical (Refs 5, 112, 148, 157, 158) or ferroelectric properties (Refs 66, 67, 102, 112, 118, 128, 129, 131, 147, 157, 159 – 164) are mainly studied, but this goes beyond the scope of this review.

1. Enantioselective heterogeneous catalysis

In spite of clearly seen importance and promise of research in this field, only a few examples of the use of homochiral metal-organic coordination polymers in enantioselective heterogeneous catalytic reactions have been reported so far.

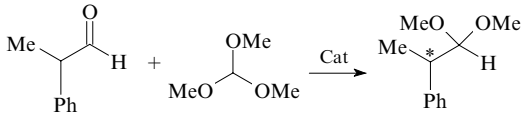
In the pioneering study,[80] a homochiral porous metal-organic coordination polymer $[H_3O]_2[Zn_3(\mu_3\text{-}O)(L24)_6]\cdot \cdot 12\,H_2O$ (**46**, commercial name POST-1) was used in asymmetric catalysis. The transesterification reaction (1) in the presence of this catalyst showed a small (~8%) excess of the *S*-enantiomer of the acetylated product when using a racemic mixture of this initial alcohol.

A terbium-based metal-organic coordination polymer $[Tb(H_2L1)(H_3L1)(H_2O)_4]$ (**1**) was studied as a catalyst in the cyanosilylation of aldehydes and the opening of cyclic anhydrides of *meso*-forms of carboxylic acids.[36] Reactions with substrates of different size and nature were carried out; however, the enantiomeric excesses (*ee*) of the products in all cases were low (a few per cent).



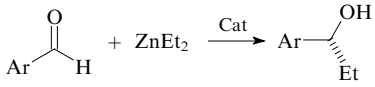
(1)

The sorption and catalytic properties of the framework compound [Zn(L26)] (**48**) were studied taking sorption of linear and cyclic aliphatic hydrocarbons and the acetylation of racemic 2-phenylpropanal with trimethylorthoformate [reaction (2)] as examples, respectively.[82] The best results obtained for reaction (2) are as follows: a substrate conversion of 60% and a product *ee* of 30%.



(2)

Compounds $[Cd_3(L11)_4(NO_3)_6]\cdot 7\,MeOH\cdot 5\,H_2O$ (**30**) and $[Cd(L11)_2(H_2O)_2](ClO_4)_2\cdot DMF\cdot 4\,MeOH\cdot 3\,H_2O$ (**31**) were used as catalysts of asymmetric alkylation of aromatic aldehydes [reaction (3)].[50]

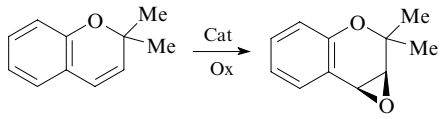


(3)

Prior to studying the catalytic properties for generation of Lewis centres in the framework, the polymers **30** and **31** were stored in vacuum and then treated with titanium(IV) isopropoxide. Hydroxyl groups of the binaphthyl ligand in positions 2 coordinate titanium with the formation of binolate complexes which do exhibit catalytic activity. For compound **30**, the maximum conversion is 99% and the enantiomeric excess is 90%. Compound **31** treated with titanium isopropoxide under identical conditions shows no catalytic properties; this was explained by the influence of steric factors.

Complex $[Cd_3Cl_6(L10)_3]\cdot Ti\cdot 4\,DMF\cdot 6\,MeOH\cdot 3\,H_2O$ obtained by post-synthetic modification of homochiral metal-organic coordination polymer **28** was studied as catalyst of diethylzinc addition to aromatic aldehydes [reaction (3)].[48] The results obtained (93% *ee* at a substrate conversion of 99%) are comparable with those obtained for the corresponding homogeneous catalyst based on binaphthol derivatives. It should be emphasized that the efficiency of the heterogeneous catalyst (in contrast to the homogeneous catalyst) abruptly decreases as the bulkiness of substituents in the substrate increases, which indicates a reaction within pores in the framework.

A coordination polymer $[Zn_2(bpdc)_2(L20)]\cdot 10\,DMF\cdot 8\,H_2O$ (**43**) catalyzes the epoxidation of alkenes [reaction (4)].[73]

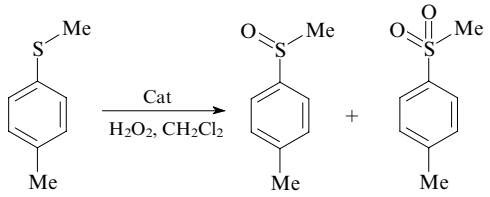


(4)

The observed *ee* value of the product of heterogeneous catalysis (82%) is comparable with the value obtained in a similar reaction with the homogeneous catalyst (88% *ee*). It was reported that the turnover number of the heterogeneous catalyst can be as high as 1430.

The coordination polymers based on a bis(catechol) derivative of the manganese(III) salen complex (L21), which presumably have a chain structure, also exhibit catalytic properties in the asymmetric epoxidation reaction [see reaction (4)].[74] Mention should be made of the author's observation that the enantiomeric excess and conversion demonstrated by all coordination polymers studied are somewhat lower but comparable with those attained with the homogeneous catalyst. It should also be noted that almost all studied homochiral metal-organic coordination polymers are rather stable under the experimental conditions.

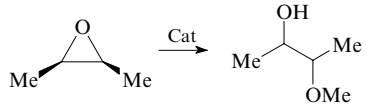
Metal-organic coordination polymers based on zinc, *viz*., $[Zn_2(bdc)((S)\text{-L49})(dmf)]$ (**99**), $[Zn_2(ndc)((R)\text{-L50})\cdot(dmf)]$ (**100**) and $[Zn_2(bpdc)((R)\text{-L50})(dmf)]$ (**101**), are efficient catalysts of the oxidation of thioethers to sulfoxides and sulfones by a 'green' oxidant H_2O_2 [reaction (5)].



(5)

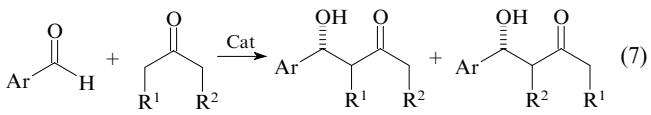
They demonstrated high conversion and regioselectivity; however, the formation of sulfoxides showed no enantioselectivity. It was experimentally proved that efficient oxidation of thioethers is observed only if the substrate can penetrate into the channels of the metal-organic framework.[123, 151] A study on the mechanism of heterogeneous catalysis showed that the activity of compound **99** is due to activation of H_2O_2 molecules on coordinatively unsaturated Zn^{2+} centres in the framework and subsequent attack of the substrate adsorbed in the voids of the framework.[165]

A metal-organic coordination polymer based on copper, aspartic acid and bridging ligand bpe — $[Cu_2((S)\text{-L29})_2\cdot(bpe)]\cdot 0.5\,H_2O$ (**79**) — was used as catalyst of methanolysis of *cis*-2,3-dimethyloxirane [reaction (6)].[125] Low *ee* values (~10%) of the product at moderate conversions (~50%) were reported.



(6)

Aldol condensation between various aromatic aldehydes and ketones [reaction (7)] on modified mesoporous catalysts MIL-101 with the L43 and L44 ligands was studied.[120]

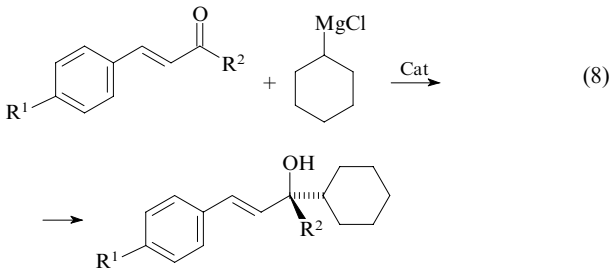


(7)

R^1, R^2 = Alk.

These are better catalysts compared to the initial framework MIL-101 or corresponding proline derivative, *viz*., the conversion reaches a value of 90% and *ee* can be as high as 80%. Additional studies using substrates whose sizes *a priori* exceed the pore size in the MIL-101 framework. The results obtained confirm the occurrence of the catalytic reaction of asymmetric synthesis within the framework.

A coordination polymer $[Cu_2(L36)Cl_2]$ (**63**) was studied as catalyst of the 1,2-addition of α,β-unsaturated ketones (8).[94]



(8)

Conversions of 93% and *ee* of 99% were reported for the methyl derivatives (R^2 = Me). However, here one deals with surface catalysis rather than catalysis in the voids of the framework.

Isoreticular mesoporous homochiral metal-organic coordination polymers based on Cu^{2+} and various derivatives of 1,1′-binaphthyltetracarboxylic acids and having channels 8 to 32 Å in diameter were treated with $Ti(OPr^i)_4$ to obtain catalysts of diethylzinc or ethyl(alkenylphenyl)-zinc addition to various aromatic aldehydes in order to synthesize chiral secondary alcohols.[53] The catalysts are stable under the reaction conditions. It was shown that the enantiomeric excess of the product depends on the ratio of the pore size in the solid metal-organic coordination polymer to the substrate size and can vary from 0% to 94%.

Chain heterometallic homochiral metal-organic coordination polymers $[Fe^{II}/Rh^{I}(L17)]X_3$ (X are various anions) were studied in the reduction of methyl-α-acetamidoacrylate, enamides and derivatives of itaconic acid resulting in chiral products.[55] It was found that the heterogeneous catalyst is at least as efficient as the homogeneous catalyst and gives products with *ee* to 97% at low loads and high turnover number of the catalyst. The dependence of the enantiomeric excess of the product on the type of the anion in the starting iron salts should be pointed out.

2. Enantioselective sorption and resolution of enantiomers

In their pioneering study, Kim and co-workers[80] reported experiments on the resolution of a racemic complex $[Ru(2,2'\text{-bipy})_3]^{2+}$ in methanol. Once the homochiral metal-organic coordination polymer $[H_3O]_2[Zn_3(\mu_3\text{-O})\cdot(HL24)_6]\cdot 12\,H_2O$ (**46**) was introduced into the solution of this complex, colourless crystals turned red-yellow; this indicated that the ruthenium complex is incorporated into the porous framework. The enantiomeric excess of the complex was 66%, as determined from circular dichroism

data and by ^{1}H NMR and IR spectroscopies. This is the first example of resolution of enantiomers using homochiral metal-organic coordination polymers.

Stereoselective sorption of metal-organic coordination polymers $[Ln(H_2L1)(H_3L1)(H_2O)_4]\cdot x\,H_2O$ (**1**) towards *trans*-1,2-diaminocyclohexane was studied.[36] The *ee* value of the product obtained using the terbium derivative was about 14%.

The coordination polymer $[Cd(L18)_2]$ (**41**)[64] has the framework with adamantane-like voids. It is also characterized by 98% selectivity of (*S*)-butan-2-ol sorption under solvothermal conditions. A study of 2-methylbutan-1-ol as substrate revealed an enantiomeric excess of only 8.5%.

The metal-organic polymer $[Cu_5Cl_6(L19)_2]\cdot EtOH$ (**42**) is formed by heating copper(I) chloride and the racemic ligand L19 in ethanol.[65] When this reaction was conducted in racemic butan-2-ol, the interlayer space of the coordination polymer was mainly occupied by the (*R*)-butan-2-ol molecules.

The sorption properties of the polymer $[Ni_3(btc)_2(3\text{-pic})_6(1,2\text{-prd})_3]\cdot 9\,(1,2\text{-Prd})\cdot 11\,H_2O$ (**51**) towards ethyl 3-hydroxybutyrate, 1,1′-binaphthyldiol and terpenes (menthone and fenchone) were studied.[86] All these substrates were sorbed by the porous material; a low stereoselectivity (8.3% *ee*) was only observed for the bulky guest (1,1′-binaphthyldiol). In other cases, no enantioselective resolution was observed.

The homochiral porous metal-organic coordination polymer $[Cd(L11)_2(H_2O)_2](ClO_4)_2\cdot 2\,DMF\cdot 3\,EtOH\cdot 5\,H_2O$ (**29**) was used for stereoselective sorption of various aromatic substrates.[49] A low enantiomeric excess (6%) was observed only for 1-phenylethanol.

Isoreticular zinc lactates and mandelates **99**–**101** exhibit good sorption properties towards chiral alcohols and sulfoxides.[123, 137, 150, 151] The highest enantiomeric excess in the sorption of aliphatic alcohols on the framework $[Zn_2(bdc)((S)\text{-L49})(dmf)]$ (**99**) is 14% for butan-1-ol. The sorption of sulfoxides is characterized by the highest *ee* values of 60% for methyl phenyl sulfoxide on compound **99**, 62% for isopropyl phenyl sulfoxide on the framework $[Zn_2(ndc)((R)\text{-L50})(dmf)]$ (**100**) and 27% for methyl 2-naphthyl sulfoxide on the framework $[Zn_2(bpdc)((R)\text{-L50})(dmf)]$ (**101**). Noticeable selectivity towards the substrate size was observed. For example, methyl 2-naphthyl sulfoxide is not sorbed into the framework of polymer **99** (*cf.* 31% *ee* for compound **100** with larger pore sizes). A *ee* of 20% for sorption of a precursor of the pharmaceutical sulforaphane $[MeSO(CH_2)_4OH]$ on the framework of compound **99** should be pointed. Quantum chemical calculations of the energy of the chiral guest (*R*- and *S*-enantiomers of methyl phenyl sulfoxides)–chiral host $\{[Zn_2(bdc)((S)\text{-L49})(dmf)]$ (**99**)$\}$ interaction were carried out. The calculated energy of the interaction of methyl phenyl sulfoxides with the chiral framework is $+9.432$ kcal mol^{-1} for the *R*-enantiomer and 1.568 kcal mol^{-1} for the *S*-enantiomer,[151] which indicates selective sorption of the *S*-form. Indeed, experimental data confirm selective sorption of the *S*-enantiomer by compound **99**. Similar quantum chemical calculations were also carried out for the precursor of sulforaphane.

High stability of compound **99** and relative ease of its synthesis allowed one to use for the first time homochiral metal-organic coordination polymers for chromatographic separation of chiral substrates.[150] A tailor-made chromatographic column showed a highly efficient resolution of alkyl aryl sulfoxides into enantiomers.

Stereoselective sorption properties of the metal-organic coordination polymer $[Ni_2((S)\text{-L29})_2(bipy)]\cdot MeOH\cdot H_2O$ (**78**) towards various aliphatic alcohols and diols were studied.[124] The best result (54% *ee*) was obtained for 2-methylpentane-2,4-diol.

Single crystals of $[Zn_6(L23)_6]\cdot 6\,THF$ (**45**) heated *in vacuo* were treated with a racemic mixture of pentan-2-ol.[79] According to X-ray diffraction data, single crystals thus formed contained the *R*-enantiomer only. A study with other alcohols revealed highly selective sorption of (*R*)-butan-2-ol and (*R*)-3-methylbutan-2-ol by compound **45**. High crystallinity of the homochiral metal-organic coordination polymer **45** and good enantioselectivity of the resolution of alcohols (*ee* to 98%) are retained after 5 catalytic cycles.

IV. Conclusion

In this review, we systematized recent advances in chemistry of homochiral porous metal-organic coordination polymers. The main advantages were achieved in the synthesis and structure determination of these compounds. The available synthetic approaches include the use of (i) optically pure, rigid bridging ligands; (ii) chiral templates or chiral polyfunctional ligands; (iii) post-synthetic modification of achiral frameworks and (iv) combination of chiral and rigid bridging ligands.

Each approach has its own advantages and drawbacks. Metal-organic coordination polymers obtained by these methods usually have permanently porous structures and extensive internal surfaces; some of them exhibit stereoselective sorption and catalytic properties. The results presented above suggest that the stereoselectivity of processes carried out using this class of compounds depends on the following factors:

1) the framework topology and the pore size (the better the size and shape correspondence between the chiral substrate and the pore the higher the stereoselectivity); and

2) the presence of accessible active catalytic sites on the internal surface of the polymer.

For instance, the best catalytic results were obtained on modified homochiral frameworks with immobilized active Lewis sites.[48, 50] It was also shown that permanent porosity is not a necessary condition for the use of metal-organic coordination polymers in the sorption or catalytic processes.[36, 64, 65, 80] Nevertheless, studies on the reasons for the onset of stereoselectivity in sorption and catalysis are scarce, while the first theoretical calculations of supramolecular interactions between chiral porous frameworks and chiral guests were reported quite recently.[151, 166]

Considering the number of examples presented here, one may think that the review is to a great extent devoted to the studies on stereoselective sorption and stereoselective catalysis on homochiral porous metal-organic coordination polymers. However, studies on the synthesis of this class of compounds are scarce compared to the total number of synthetic publications. This is to a great extent due to the fact that homochiral porous coordination polymers are mainly synthesized using complex, optically pure organic ligands, which significantly reduces the potential of research on their catalytic and sorption properties and moreover their application in large-scale processes. In this connection,

the development of versatile methods of synthesis of homochiral porous metal-organic coordination polymers based on the available optically pure reagents is still topical. In this connection, mention may be made of a recently proposed method for the synthesis of homochiral metal-organic coordination polymers based on combination of the properties of chiral and rigid bridging ligands (see Fig. 38). The technique allows one to vary with ease such properties of the synthesized frameworks, as the pore size, the nature of optical and catalytic sites and hydrophilicity/hydrophobivity of the internal surface. This approach may appear to be promising for the synthesis of new families of isoreticular homochiral porous metal-organic coordination polymers for enantioselective catalysis and resolution.

Several papers [167–175] on the title subject have appeared in the course of preparation of the manuscript.

The authors express their gratitude to the Russian Foundation for Basic Research for continuous financial support of our research in the field of chemistry of metal-organic coordination polymers (Project Nos 07-03-00436, 07-03-91208, 08-03-12007, 09-03-12112, 09-03- 90414 and 11-03-00112).

References

1. B F Hoskins, R Robson *J. Am. Chem. Soc.* **112** 1546 (1990)
2. O M Yaghi, H Li, C Davis, D Richardson, T L Groy *Acc. Chem. Res.* **31** 474 (1998)
3. R Robson *J. Chem. Soc., Dalton Trans.* 3735 (2000)
4. M Eddaoudi, J Kim, N Rosi, D Vodak, J Wachter, M O'Keeffe, O M Yaghi *Science* **295** 469 (2002)
5. C Janiak *Dalton Trans.* 2781 (2003)
6. S Kitagawa, R Kitaura, S-I Noro *Angew. Chem., Int. Ed.* **43** 2334 (2004)
7. H Li, M Eddaoudi, M O'Keeffe, O M Yaghi *Nature (London)* **402** 276 (1999)
8. S Horike, S Shimomura, S Kitagawa *Nature Chem.* **1** 695 (2009)
9. O K Farha, J T Hupp *Acc. Chem. Res.* **43** 1166 (2010)
10. L J Murray, M Dinca, J R Long *Chem. Soc. Rev.* **38** 1294 (2009)
11. J R Li, R J Kuppler, H C Zhou *Chem. Soc. Rev.* **38** 1477 (2009)
12. M Dinca, A F Yu, J R Long *J. Am. Chem. Soc.* **128** 27 (2006)
13. A K Cheetham, C N R Rao, R K Feller *Chem. Commun.* 4780 (2006)
14. K M Thomas *Dalton Trans.* 1487 (2009)
15. S Keskin, J Liu, R B Rankin, J K Johnson, D S Sholl *Ind. Eng. Chem. Res.* **48** 2355 (2009)
16. S Kitagawa, R Matsuda *Coord. Chem. Rev.* **251** 2490 (2007)
17. A J Fletcher, K M Thomas, M J Rosseinsky *J. Solid State Chem.* **178** 2491 (2005)
18. B Xiao, Q C Yuan *Particuology* **7** 129 (2009)
19. C Z Mu, F Xu, W Lei *Prog. Chem.* **19** 1345 (2007)
20. D Y Hong, Y K Hwang, C Serre, G Ferey, J S Chang *Adv. Funct. Mater.* **19** 1537 (2009)
21. S Bureekaew, S Shimomura, S Kitagawa *Sci. Technol. Adv. Mater.* **9** 14108 (2008)
22. A Phan, C J Doonan, F J Uribe-Romo, C B Knobler, M O'Keeffe, O M Yaghi *Acc. Chem. Res.* **43** 58 (2010)
23. R Custelcean, B A Moyer *Eur. J. Inorg. Chem.* 1321 (2007)
24. D Maspoch, D Ruiz-Molina, J Veciana *Chem. Soc. Rev.* **36** 770 (2007)
25. B L Chen, S C Xiang, G D Qian *Acc. Chem. Res.* **43** 1115 (2010)
26. T Uemura, S Horike, S Kitagawa *Chem. – Asian J.* **1** 36 (2006)
27. G Ferey, C Mellot-Draznieks, C Serre, F Millange, J Dutour, S Surble, I Margiolaki *Science* **309** 2040 (2005)
28. H Furukawa, N Ko, Y B Go, N Aratani, S B Choi, E Choi, A O Yazaydin, R Q Snurr, M O'Keeffe, J Kim, O M Yaghi *Science* **329** 424 (2010)
29. K A Kovalenko, Candidate Thesis in Chemical Sciences, Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 2010
30. B Kesanli, W Lin *Coord. Chem. Rev.* **246** 305 (2003)
31. W Lin *MRS Bull.* **32** 544 (2007)
32. K P Brilyakov, E P Talsi *Chem. Phys. Res. J.* **1** 47 (2008)
33. L Ma, C Abney, W Lin *Chem. Soc. Rev.* **38** 1248 (2009)
34. R E Morris, X Bu *Nature Chem.* **2** 353 (2010)
35. G B Bokii *Kristallokhimiya* (Crystallochemistry) (Moscow: Nauka, 1971)
36. O R Evans, H L Ngo, W Lin *J. Am. Chem. Soc.* **123** 10395 (2001)
37. O R Evans, D R Manke, W Lin *Chem. Mater.* **14** 3866 (2002)
38. Y Cui, H L Ngo, P S White, W Lin *Chem. Commun.* 1666 (2002)
39. Y Cui, O R Evans, H L Ngo, P S White, W Lin *Angew. Chem., Int. Ed.* **41** 1159 (2002)
40. H L Ngo, W Lin *J. Am. Chem. Soc.* **124** 14298 (2002)
41. Y Cui, H L Ngo, P S White, W Lin *Inorg. Chem.* **42** 652 (2003)
42. Y Cui, H L Ngo, P S White, W Lin *Chem. Commun.* 994 (2003)
43. C-D Wu, W Lin *Dalton Trans.* 4563 (2006)
44. Y Cui, S J Lee, W Lin *J. Am. Chem. Soc.* **125** 6014 (2003)
45. C-D Wu, W Lin *Inorg. Chem.* **44** 1178 (2005)
46. C-D Wu, W Lin *Angew. Chem., Int. Ed.* **44** 1958 (2005)
47. C-D Wu, L Zhang, W Lin *Inorg. Chem.* **45** 7278 (2006)
48. C-D Wu, A Hu, L Zhang, W Lin *J. Am. Chem. Soc.* **127** 8940 (2005)
49. C-D Wu, W Lin *Chem. Commun.* 3673 (2005)
50. C-D Wu, W Lin *Angew. Chem., Int. Ed.* **46** 1075 (2007)
51. L Ma, W Lin *J. Am. Chem. Soc.* **130** 13834 (2008)
52. L Ma, W Lin *Angew. Chem., Int. Ed.* **48** 3637 (2009)
53. L Ma, J M Falkowski, C Abney, W Lin *Nature Chem.* **2** 838 (2010)
54. C-D Wu, L Ma, W Lin *Inorg. Chem.* **47** 11446 (2008)
55. L Yu, Z Wang, J Wu, S Tu, K Ding *Angew. Chem., Int. Ed.* **49** 3627 (2010)
56. Y Cui, H L Ngo, W Lin *Chem. Commun.* 1388 (2003)
57. C-D Wu, H L Ngo, W Lin *Chem. Commun.* 1588 (2004)
58. R Wang, L Xu, X Li, Y Li, Q Shi, Z Zhou, M Hong, A S C Chan *Eur. J. Inorg. Chem.* 1595 (2004)
59. T J Burchell, R J Puddephatt *Inorg. Chem.* **45** 650 (2006)
60. T J Burchell, R J Puddephatt *Inorg. Chem.* **44** 3718 (2005)
61. C A Wheaton, M C Jennings, R J Puddephatt *J. Am. Chem. Soc.* **128** 15370 (2006)
62. X Ouyang, Z Chen, X Liu, Y Yang, M Deng, L Weng, Y Zhou, Y Jia *Inorg. Chem. Commun.* **11** 948 (2008)
63. Q Gao, F-L Jiang, M-Y Wu, Y-G Huang, W Wei, M-C Hong *Cryst. Growth Des.* **10** 184 (2010)
64. R-G Xiong, X-Z You, B F Abrahams, Z Xue, C-M Che *Angew. Chem., Int. Ed.* **113** 4554 (2001)
65. Y-R Xie, X-S Wang, H Zhao, J Zhang, L-H Weng, C-Y Duan, R-G Xiong, X-Z You, Z-L Xue *Organometallics* **22** 4396 (2003)
66. H Zhao, Z-R Qu, Q Ye, B F Abrahams, Y-P Wang, Z-G Liu, Z Xue, R-G Xiong, X-Z You *Chem. Mater.* **15** 4166 (2003)
67. Z-R Qu, Z-F Chen, J Zhang, R-G Xiong, B F Abrahams, Z-L Xue *Organometallics* **22** 2814 (2003)
68. Y-M Song, Q Ye, Y-Z Tang, Q Wu, R-G Xiong *Cryst. Growth Des.* **5** 1603 (2005)
69. Y-Z Tang, X-F Huang, Y-M Song, P W H Chan, R-G Xiong *Inorg. Chem.* **45** 4868 (2006)
70. E M McGarrigle, D G Gilheany *Chem. Rev.* **105** 1563 (2005)

71. W Zhang, J L Loebach, S R Wilson, E N Jacobsen *J. Am. Chem. Soc.* **112** 2801 (1990)
72. K P Bryliakov, E P Talsi *Angew. Chem., Int. Ed.* **43** 5228 (2004)
73. S-H Cho, B Ma, S T Nguyen, J T Hupp, T E Albrecht-Schmitt *Chem. Commun.* 2563 (2006)
74. S-H Cho, T Gadzikwa, M Afshari, S T Nguyen, J T Hupp *Eur. J. Inorg. Chem.* 4863 (2007)
75. Y-M Jeon, J Heo, C A Mirkin *J. Am. Chem. Soc.* **129** 7480 (2007)
76. G Li, W Yu, Y Cui *J. Am. Chem. Soc.* **130** 4582 (2008)
77. M Oh, C A Mirkin *Angew. Chem., Int. Ed.* **45** 5492 (2006)
78. M Oh, C A Mirkin *Nature (London)* **438** 651 (2005)
79. A Bhunia, P W Roesky, Y Lan, G E Kostakis, A K Powell *Inorg. Chem.* **48** 10483 (2009)
80. J S Seo, D Whang, H Lee, S I Jun, J Oh, Y J Jeon, K Kim *Nature (London)* **404** 982 (2000)
81. N G Pschirer, D M Ciurtin, M D Smith, U H F Bunz, H-C zur Loye *Angew. Chem., Int. Ed.* **41** 583 (2002)
82. A Monge, N Snejko, E Gutierrez-Puebla, M Medina, C Cascales, C Ruiz-Valero, M Iglesias, B Gomez-Lor *Chem. Commun.* 1291 (2005)
83. S S Iremonger, P D Southon, C J Kepert *Dalton Trans.* 6103 (2008)
84. K Gedrich, I Senkovska, I A Baburin, U Mueller, O Trapp, S Kaskel *Inorg. Chem.* **49** 4440 (2010)
85. C J Kepert, T J Prior, M J Rosseinsky *J. Am. Chem. Soc.* **122** 5158 (2000)
86. D Bradshaw, T J Prior, E J Cussen, J B Claridge, M J Rosseinsky *J. Am. Chem. Soc.* **126** 6106 (2004)
87. E V Anokhina, A J Jacobson *J. Am. Chem. Soc.* **126** 3044 (2004)
88. E V Anokhina, Y B Go, Y Lee, T Vogt, A J Jacobson *J. Am. Chem. Soc.* **128** 9957 (2006)
89. Q Yue, J Yang, G-H Li, G-D Li, J-S Chen *Inorg. Chem.* **45** 4431 (2006)
90. H-Y Liu, B Zhao, W Shi, Z-J Zhang, P Cheng, D-Z Liao, S-P Yan *Eur. J. Inorg. Chem.* 2599 (2009)
91. Y Xie, Y Yan, H-H Wu, G-P Yong, Y Cui, Z-Y Wang, L Pan, J Li, R Fan, R-P Li, Y-C Tian, G-Q Pan, L-S Sheng, X Li *Inorg. Chim. Acta* **360** 1669 (2007)
92. T-T Luo, L-Y Hsu, C-C Su, C-H Ueng, T-C Tsai, K-L Lu *Inorg. Chem.* **46** 1532 (2007)
93. H Y Lee, J Park, M S Lah, J-I Hong *Cryst. Growth Des.* **8** 587 (2008)
94. M Wang, M-H Xie, C-D Wu, Y-G Wang *Chem. Commun.* 2396 (2009)
95. J A Rood, W C Boggess, B C Noll, K W Henderson *J. Am. Chem. Soc.* **129** 13675 (2007)
96. P Thuery *Eur. J. Inorg. Chem.* 3646 (2006)
97. Y-W Sheng, Y Wang, T-A Okamura, W-Y Sun, N Ueyama *Inorg. Chem. Commun.* **10** 432 (2007)
98. C M Fitchett, P J Steel *Dalton Trans.* 4886 (2006)
99. J Zhang, S Chen, X Bu *Angew. Chem., Int. Ed.* **47** 5434 (2008)
100. J Zhang, S Chen, A Zingiryan, X Bu *J. Am. Chem. Soc.* **130** 17246 (2008)
101. J Zhang, S Chen, T Wu, P Feng, X Bu *J. Am. Chem. Soc.* **130** 12882 (2008)
102. W Zhang, R-G Xiong, S D Huang *J. Am. Chem. Soc.* **130** 10468 (2008)
103. S Chen, J Zhang, X Bu *Inorg. Chem.* **48** 6356 (2009)
104. R E Norman, N J Rose, R E Stenkamp *J. Chem. Soc., Dalton Trans.* 2905 (1987)
105. S Thushari, J A K Cha, H H-Y Sung, S S-Y Chui, A L-F Leung, Y-F Yen, I D Williams *Chem. Commun.* 5515 (2005)
106. J A Rood, B C Noll, K W Henderson *J. Solid State Chem.* **183** 270 (2010)
107. P Thuery *CrystEngComm* **9** 460 (2007)
108. P Zhu, W Gu, L-Z Zhang, X Liu, J-L Tian, S-P Yan *Eur. J. Inorg. Chem.* 2971 (2008)
109. L J Bostelaar, R A G D Graaff, F B Hulsbergen, J Reedijk, W M H Sachtler *Inorg. Chem.* **23** 2294 (1984)
110. M O Keeffe, M A Peskov, S J Ramsden, O M Yaghi *Acc. Chem. Res.* **41** 1782 (2008)
111. Z-R Qu, H Zhao, X-S Wang, Y-H Li, Y-M Song, Y-j Liu, Q Ye, R-G Xiong, B F Abrahams, Z-L Xue, X-Z You *Inorg. Chem.* **42** 7710 (2003)
112. Y-R Xie, H Zhao, X-S Wang, Z-R Qu, R-G Xiong, X Xue, Z Xue, X-Z You *Eur. J. Inorg. Chem.* 3712 (2003)
113. Y Zhang, M K Saha, I Bernal *CrystEngComm* **5** 34 (2003)
114. X Shi, G Zhu, S Qiu, K Huang, J Yu, R Xu *Angew. Chem., Int. Ed.* **43** 6482 (2004)
115. Q Ye, Y-H Li, Q Wu, Y-M Song, J-X Wang, H Zhao, R-G Xiong, Z Xue *Chem. – Eur. J.* **11** 988 (2005)
116. H-T Zhang, Y-Z Li, T-W Wang, E N Nfor, H-Q Wang, X-Z You *Eur. J. Inorg. Chem.* 3532 (2006)
117. L Zhang, B-W Sun *Acta Crystallogr., Sect. E* **64** 1 (2008)
118. D Sarma, K V Ramanujachary, S E Lofand, T Magdaleno, S Natarajan *Inorg. Chem.* **48** 11660 (2009)
119. S Banerjee, N N Adarsh, P Dastidar *CrystEngComm* **11** 746 (2009)
120. M Banerjee, S Das, M Yoon, H J Choi, M H Hyun, S M Park, G Seo, K Kim *J. Am. Chem. Soc.* **131** 7524 (2009)
121. J W Yang, C Chandler, M Stadler, D Kampen, B List *Nature (London)* **452** 453 (2008)
122. B List, R A Lerner, C F Barbas *J. Am. Chem. Soc.* **122** 2395 (2000)
123. D N Dybtsev, A L Nuzhdin, H Chun, K P Bryliakov, E P Talsi, V P Fedin, K Kim *Angew. Chem., Int. Ed.* **45** 916 (2006)
124. R Vaidhyanathan, D Bradshaw, J-N Rebilly, J P Barrio, J A Gould, N G Berry, M J Rosseinsky *Angew. Chem., Int. Ed.* **45** 6495 (2006)
125. M J Ingleson, J P Barrio, J Bacsa, C Dickinson, H Park, M J Rosseinsky *Chem. Commun.* 1287 (2008)
126. J P Barrio, J-N Rebilly, B Carter, D Bradshaw, J Bacsa, A Y Ganin, H Park, A Trewin, R Vaidhyanathan, A I Cooper, J E Warren, M J Rosseinsky *Chem. – Eur. J.* **14** 4521 (2008)
127. M P Yutkin, M S Zavakhina, D G Samsonenko, D N Dybtsev, V P Fedin *Izv. Akad. Nauk, Ser. Khim.* 719 (2010) [a]
128. P Zhu, W Gu, F-Y Cheng, X Liu, J Chen, S-P Yan, D-Z Liao *CrystEngComm* **10** 963 (2008)
129. F-P Huang, H-Y Li, J-L Tian, W Gu, Y-M Jiang, S-P Yan, D-Z Liao *Cryst. Growth Des.* **9** 3191 (2009)
130. M J Ingleson, J Bacsa, M J Rosseinsky *Chem. Commun.* 3036 (2007)
131. F Luo, Y-T Yang, Y-X Che, J-M Zheng *CrystEngComm* **10** 1613 (2008)
132. Z Chen, Y Su, W Xiong, L Wang, F Liang, M Shao *CrystEngComm* **11** 318 (2009)
133. W Xiong, Y Su, Z Chen, F Liang *Acta Crystallogr., Sect. C* **65** m56 (2009)
134. D L Reger, J Horger, M D Smith, G J Long *Chem. Commun.* 6219 (2009)
135. D N Dybtsev, M P Yutkin, E V Peresypkina, A V Virovets, C Serre, G Ferey, V P Fedin *Inorg. Chem.* **46** 6843 (2007)
136. D N Dybtsev, M P Yutkin, V P Fedin *Izv. Akad. Nauk, Ser. Khim.* 2179 (2009) [a]
137. M P Yutkin, Candidate Thesis in Chemical Sciences, Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 2010
138. V A Logvinenko, D N Dybtsev, M P Yutkin, V P Fedin, S Yan, D-Z Liao *CrystEngComm* **10** 963 (2008)
139. J A Rood, B C Noll, K W Henderson *Main Group Chem.* **8** 237 (2009)

140. J Zhang, E Chew, S Chen, J T H Pham, X Bu *Inorg. Chem.* **47** 3495 (2008)
141. J Zhang, X Bu *Angew. Chem., Int. Ed.* **46** 6115 (2007)
142. L Wang, W You, W Huang, C Wang, X-Z You *Inorg. Chem.* **48** 4295 (2009)
143. M-H Zeng, B Wang, X-Y Wang, W-X Zhang, X-M Chen, S Gao *Inorg. Chem.* **45** 7069 (2006)
144. J Zhang, S Chen, H Valle, M Wong, C Austria, M Cruz, X Bu *J. Am. Chem. Soc.* **129** 14168 (2007)
145. J Zhang, Y-G Yao, X Bu *Chem. Mater.* **19** 5083 (2007)
146. J Zhang, T Wu, P Feng, X Bu *Chem. Mater.* **20** 5457 (2008)
147. X-Q Liang, D-P Li, X-H Zhou, Y Sui, Y-Z Li, J-L Zuo, X-Z You *Cryst. Growth Des.* **9** 4872 (2009)
148. L-L Liang, S-B Ren, J Zhang, Y-Z Li, H-B Du, X-Z You *Cryst. Growth Des.* **10** 1307 (2010)
149. Y V Mironov, N G Naumov, K A Brylev, O A Efremova, V E Fedorov, K Hegetschweiler *Angew. Chem., Int. Ed.* **43** 1297 (2004)
150. A L Nuzhdin, D N Dybtsev, K P Bryliakov, E P Talsi, V P Fedin *J. Am. Chem. Soc.* **129** 12958 (2007)
151. D N Dybtsev, M P Yutkin, D G Samsonenko, V P Fedin, A L Nuzhdin, A A Bezrukov, K P Bryliakov, E P Talsi, R V Belosludov, H Mizuseki, Y Kawazoe, O S Subbotin, V R Belosludov *Chem.–Eur. J.* **16** 10348 (2010)
152. H-Q Hao, W-T Liu, W Tan, Z Lin, M-L Tong *Cryst. Growth Des.* **9** 457 (2008)
153. L Sbircea, N D Sharma, W Clegg, R W Harrington, P N Horton, M B Hursthouse, D C Apperley, D R Boyd, S L James *Chem. Commun.* 5538 (2008)
154. A Zingiryan, J Zhang, X Bu *Inorg. Chem.* **47** 8607 (2008)
155. O Sereda, H Stoeckli-Evans, O Dolomanov, Y Filinchuk, P Pattison *Cryst. Growth Des.* **9** 7 3168 (2009)
156. C Livage, N Guillou, P Rabu, P Pattison, J Marrot, G Ferey *Chem. Commun.* 4551 (2009)
157. S Q Zang, Y Su, Y Z Li, Z P Ni, Q J Meng *Inorg. Chem.* **45** 174 (2006)
158. R Wang, L Xu, J Ji, Q Shi, Y Li, Z Zhou, M Hong, A S C Chan *Eur. J. Inorg. Chem.* 751 (2005)
159. L-M Duan, F-T Xie, X-Y Chen, Y Chen, Y-K Lu, P Cheng, J-Q Xu *Cryst. Growth Des.* **6** 1101 (2006)
160. A R Geisheimer, M J Katz, R J Batchelor, D B Leznoff *CrystEngComm* **9** 1078 (2007)
161. Z-G Gu, X-H Zhou, Y-B Jin, R-G Xiong, J-L Zuo, X-Z You *Inorg. Chem.* **46** 5462 (2007)
162. T Hang, D-W Fu, Q Ye, H-Y Ye, R-G Xiong, S D Huang *Cryst. Growth Des.* **9** 2054 (2009)
163. Z-R Qu, Q Ye, H Zhao, D-W Fu, H-Y Ye, R-G Xiong, T Akutagawa, T Nakamura *Chem.–Eur. J.* **14** 3452 (2008)
164. Q Ye, D-W Fu, H Tian, R-G Xiong, P W H Chan, S D Huang *Inorg. Chem.* **47** 772 (2008)
165. A L Nuzhdin, D N Dybtsev, V P Fedin, G A Bukhtiyarova *Dalton Trans.* 10481 (2009)
166. X Bao, L J Broadbelt, R Q Snurr *Phys. Chem. Chem. Phys.* **12** 6466 (2010)
167. F Song, C Wang, J M Falkowski, L Ma, W Lin *J. Am. Chem. Soc.* **132** 15390 (2010)
168. D Dang, P Wu, C He, Z Xie, C Duan *J. Am. Chem. Soc.* **132** 14321 (2010)
169. L Ma, C-D Wu, M M Wanderley, W Lin *Angew. Chem., Int. Ed.* **49** 8244 (2010)
170. R A Smaldone, R S Forgan, H Furukawa, J J Gassensmith, A M Z Slawin, O M Yaghi, J F Stoddart *Angew. Chem., Int. Ed.* **49** 8630 (2010)
171. F Song, C Wang, W Lin *Chem. Commun.* 8256 (2011)
172. Y Huang, T Liu, J Lin, J Lü, Z Lin, R Cao *Inorg. Chem.* **50** 2191 (2011)
173. S-C Xiang, Z Zhang, C-G Zhao, K Hong, X Zhao, D-R Ding, M-H Xie, C-D Wu, M C Das, R Gill, K M Thomas, B Chen *Nature Commun.* **2** 204 (2011)
174. X Xi, Y Fang, T Dong, Y Cui *Angew. Chem., Int. Ed.* **50** 1154 (2011)
175. J M Falkowski, C Wang, S Liu, W Lin *Angew. Chem., Int. Ed.* **50** 8674 (2011)

[a] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*