PERSPECTIVE

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Engineering coordination polymers towards applications

Christoph Janiak

Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany. E-mail: janiak@uni-freiburg.de; Fax: 49 761 2036147; Tel: 49 761 2036127

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The development in the field of coordination polymers or metal-organic coordination networks, MOCNs (metal-organic frameworks, MOFs) is assessed in terms of property investigations in the areas of catalysis, chirality, conductivity, luminescence, magnetism, spin-transition (spin-crossover), non-linear optics (NLO) and porosity or zeolitic behavior upon which potential applications could be based.

Introduction

What are "coordination polymers"?

Coordination polymers,[1] also known as metal-organic coordination networks (MOCNs) or metal-organic frameworks (MOFs), are metal-ligand compounds that extend "infinitely" into one, two or three dimensions (1D, 2D or 3D, respectively) *via* more or less covalent metal-ligand bonding (Fig. 1).[2] The ligand must be a bridging organic group. At least in one extended dimension the metal atoms must solely be bridged by this organic ligand. Furthermore, at least one carbon atom must lie between the donor atoms. The last requirement excludes groups such as organyloxides (RO$^-$), organophosponates (RPO$_3^{2-}$) or organosulfonates (RSO$_3^-$), which bridge with their one "inorganic" end group only, from giving rise to coordination polymers. Infinite metal-ligand assemblies where the metal-organic connectivity is interrupted by "inorganic" bridges, such as –(R,H)O–, –Cl–, –CN–, –N$_3$–, –(R,O)PO$_3$– and –(R,O)SO$_3$– or where an extended inorganic metal-ligand network is lined by only terminal organic ligands are called organic–inorganic hybrid-materials (Fig. 2).[3] This differentiation is more than a formality. It is the bridging organic ligands which allow for the large diversity in the topologies and possible properties of the metal-organic coodination networks.

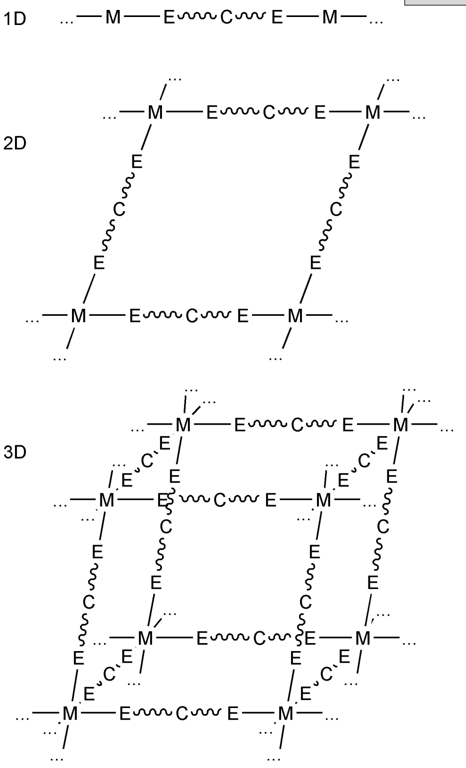

Fig. 1 Schematic representation of the definition of 1D, 2D or 3D coordination polymers having organic bridging ligands with at least one carbon atom in-between the donor atoms (E). Donor atoms (E) can be O, N, S, Se *etc.*

Weaker noncovalent interactions, such as hydrogen bonding or π–π stacking are important for the packing of the one-dimensional chains, two-dimensional nets and three-dimensional frameworks.[4,5] However, the multi-dimensional *supra*-molecular architectures of metal complexes which are created by purely hydrogen bonding (Fig. 2)[6–9] are not viewed here as coordination polymers. Also, metallo-macrocycles, metallosupramolecular cubes, cages or capsules,[10–12] metallocatenanes,[13] coordination clusters[14] or helicates[15] may be large metal-ligand assemblies, yet they are still finite *super-* (and possibly also *supra-*) molecular metal-ligand complexes and as such will not be the subject of this Perspective.[16]

Coordination polymers are most often not soluble as such.[17] The 1D, 2D and 3D metal-ligand structures have to degradate upon dissolution into metal-solvate/ligand complexes and the free ligand. Hence, any solution properties which are sometimes reported for coordination polymers are by no means characteristic of the solid-state material. Sometimes oligomeric fragments are suggested in solution, occasionally substantiated by molar mass measurements,[18] yet their exact nature remains

Christoph Janiak was born in Berlin, Germany in 1961. He studied chemistry at the TU Berlin and the University of Oklahoma in Norman under the auspices of Prof. Jerold J. Zuckerman (MSc work) and Prof. Herbert Schumann (PhD work). After postdoctoral work with Prof. Roald Hoffmann at Cornell University and with the polyolefin division of BASF AG at Ludwigshafen, he returned to the TU Berlin for his "Habilitation" which was concluded in 1995. In 1996 he moved to the University of Freiburg where he is now a Professor of Inorganic and Analytical Chemistry. The research interests of Christoph Janiak extend from metal-ligand coordination polymers over porous structures and supramolecular coordination chemistry (stacking, hydrogen bonding) to catalysis with coordination compounds and olefin polymerization with single-site catalysts.

Christoph Janiak

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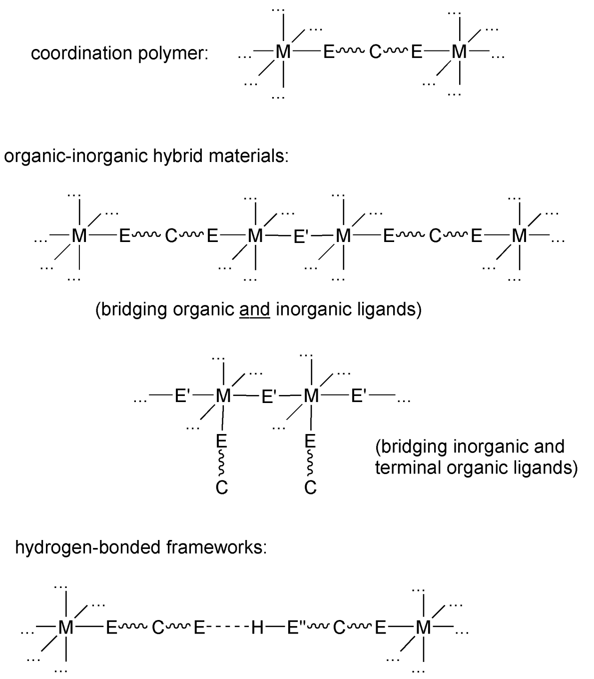


Fig. 2 Schematic representation of a coordination polymer *versus* other extended metal-ligand structures (only one direction shown). Donor atoms (E, E′) can be O, N, S, Se *etc* (E″ mainly O and N).

often elusive. Generally, little is known about potential metal-ligand species which may preform in solution before assembling to a coordination polymer. The insolubility and often melting with degradation limits the processability of coordination polymers into films, fibers or objects of a desired shape—different from the behavior of organic polymers. The use of the term polymer may be misleading in this respect as to many people it implies a processability familiar from organic polymers. The only compounds which could be viewed as soluble and processable "coordination polymers" are organometallic polymers, *e.g.* poly(ferrocenylsilanes)[19] or poly(metallaynes),[20] where the metal centers are linked by organic groups through direct M–C bonds. We will, however, not discuss this surely interesting novel class of transition-metal containing macromolecules within the scope of this article.

The scope of this Perspective

The last decade has seen enormous research efforts in the syntheses and studies of coordination polymers. The field of coordination polymers continues to expand exponentially. Legitimately, a major portion of work dealing with coordination polymers still describes and analyzes the metal-ligand and packing geometry through single-crystal X-ray structural investigations in terms of *crystal engineering*, structure design or control of architecture.[2,4,5,21–24] Considering the large number of papers published, a complete review of all reported structures of coordination polymers is outside the scope of this Perspective. Instead, emphasis is placed on the investigations of properties and potential applications of coordination polymers. This Perspective gives a summary of the concepts behind the syntheses and structural studies of metal-ligand coordination polymers. This Perspective will give a cross-section of the functionally oriented work involving coordination polymers.

The ligands in coordination polymers

The ligands used in the construction of coordination polymers have to bridge between metal ions. This requires usually multidentate ligands with two or more donor atoms. Such *bridging* ligands are called di-, tri-, tetratopic depending on the number of donor atoms. Of special importance are *rigid* bridging ligands since they allow for a certain control of the steric consequences in the assembly process. The diversity of organic components is, of course, the basis for the variety in structural topologies (which will not be covered here).[2,4] By carefully selecting the organic ligand one also aims to tune the physical properties and, thus, realize various applications, such as catalysis, electrical conductivity, luminescence, magnetism, non-linear optics or zeolitic behavior (to be discussed below). Popular ligands in property related work of metal coordination polymers are depicted in Fig. 3. Generally, *nitrogen-* and *oxygen-donor* ligands feature prominently in the construction of coordination polymers.[5,22–28] Considerable efforts are devoted to the synthesis of new ligand systems.

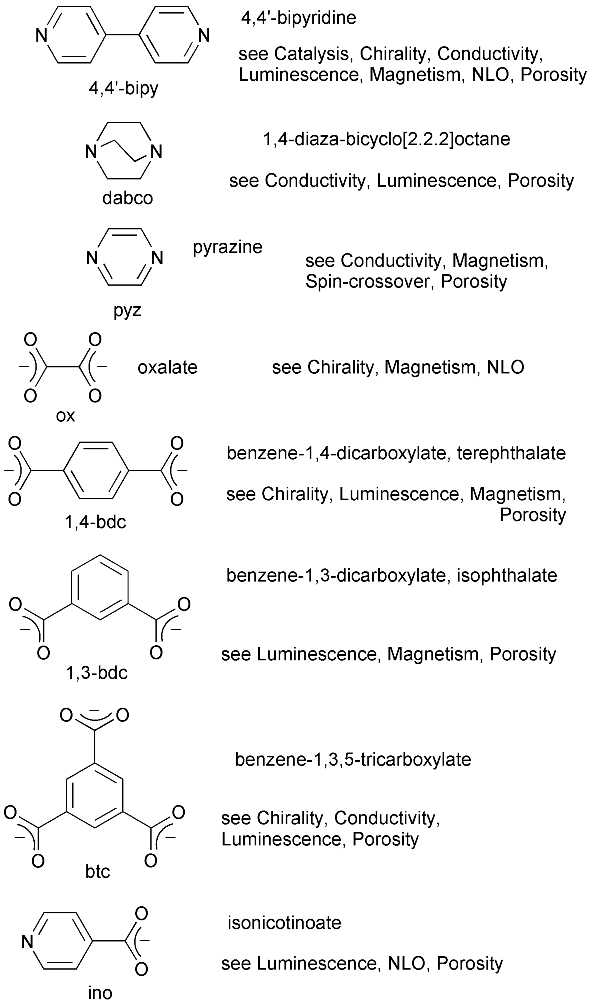


Fig. 3 Frequently encountered ligands in different areas of property related work of coordination polymers.

The compound 4,4′-bipyridine (4,4′-bipy) is a prominent example for a prototypical bridging ligand. Tailored derivatives of 4,4′-bipyridine ligands with various spacers between the bipyridine functions (*cf. e.g.* L^{10}, L^{17}, L^{18}, L^{26}, L^{27}, L^{65}, L^{66}) are attractive molecular building blocks because they effectively form diverse architectures such as one-dimensional chains,[29] and ladders,[30] two-dimensional grids[31] and three-dimensional frameworks[32] with the metal connectors.[27,28,33]

Many of the coordination polymeric structures are not easily depicted and require substantial space. Thus, we refrained from showing the multi-dimensional structures of the compounds discussed below but point only to important features where necessary and appropriate. We have only drawn the ligands to allow the reader to visualize the organic building blocks which may give rise to certain properties of the metal-ligand compound.

The theorem “solid-state architecture determines function” is the driving force behind the desire to rationally design and synthesize solid-state materials through a controlled assembly of molecular components.[4,16,34,35] The “golden-rule” in crystal engineering is that the crystal architecture can be determined by the strength and directionality of covalent[22–24,36] and non-covalent intermolecular interactions.[2,4,5,9,37] A crystal structure can in principle be regarded as a manifestation of self-assembly and self-organization.

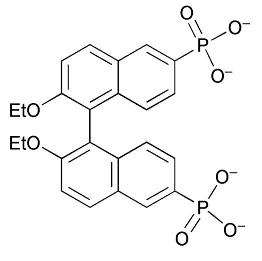
The use of metal atoms in coordination polymers offers several possible advantages over purely organic chains, grids or frameworks which are organized by non-covalent interactions:[38] Covalent metal-ligand (coordinative) bonds are stronger than hydrogen bonds. Metal-ligand bonds have more directionality than other weak interactions, such as π–π stacking[39] *etc*. An attractive feature of metal atoms is the availability of orthogonal (90°) angles for the construction of polymeric architectures.[40] Appropriate stopper ligands can restrict the number of metal coordination sites to less than the usual four or six. Together with a difference in size, hardness/softness, ligand-field stabilization energy[41] of the metal ions and various coordination modes (octahedral, tetrahedral, square planar *etc.*) this provides already for a wide range of construction possibilities. The metal atoms in coordination polymers may be thought of as assembling and templating joints for the organic bridging ligands. The shape of the metal building unit can be controlled with a metal–terminal-ligand system that exhibits a desired coordination geometry. Several metal ions may also be aggregated into larger units by appropriate multidentate linkers to serve as secondary building units (SBUs) for the overall framework.[24]

Still, an accurate prediction of the overall crystal structure is usually not possible.[42] One obstacle is the weak but numerous non-covalent interactions and their poor directionality involving the ligands and non-covalently bound anions, cations as well as solvent (guest) molecules. A metal-ligand combination can give rise to two or more different structures, even with the same stoichiometry of all components. This is termed polymorphism or supramolecular isomerism.[2,4,36] Subtle factors from the crystallization conditions, such as solvent, temperature, time, concentration, anions, pH-value play a role.[36] Thus, considerable research energy is dedicated towards understanding the self-assembly process between metal ions or secondary building units derived therefrom[24] and multidentate ligands.[2,4,22,23,25,27,28,33,36] The design and the properties of the ligand itself can be a research initiative of its own. The synthesis or self-organization of coordination polymers is achieved by combining the appropriate metal salt and ligand in a suitable solvent under mild or at the most hydrothermal[43] conditions.[44] Even though much effort is still devoted to the preparation and structure determination of a crystalline sample, a final goal is to design properties of the polymeric assemblies of transition-metal complexes with applications to material science as *catalytic*, *conductive*, *luminescent*, *magnetic*, *spin-transition*, *non-linear optical* or *porous* materials.[45]

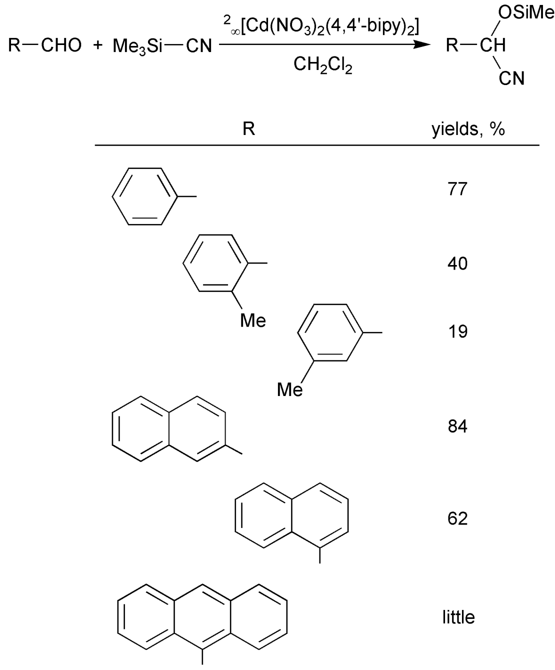
Catalysis

The porous nature of some coordination polymers (see also under *porosity*) and/or the presence of possibly catalytically active transition-metal centers is seen as the basis of size- and shape-selective catalytic applications of such materials. This idea follows the use of zeolites[46] or modified open-structure microporous aluminophosphates (AlPOs).[47] Few examples are known, so far, with coordination polymers. A meaningful catalytic study must include investigation of the liquid phase supernatant over the solid-state catalyst material after a catalytic cycle. This has to ensure that the coordination polymer does not partly dissolve and degradate so to exclude that it is its components which act as a homogeneous catalyst in solution.

The 2D square network material $^{2}_{\infty}[\mathrm{Cd(NO_3)_2(4,4'\text{-}bipy)_2}]$[†] catalyzes the cyanosilylation of aldehydes (eqn. (1)). No reaction took place with either $\mathrm{Cd(NO_3)_2}$ or 4,4′-bipy alone. A shape specificity towards the aldehyde was manifested in the product yield (see eqn. (1)) and ascribed to the cavity size of the network.[48] The homochiral 2D lanthanoid phosphonates $^{2}_{\infty}\{[\mathrm{Ln(H_2L^1)(H_3L^1)(H_2O)_4}]\cdot x\mathrm{H_2O}\}$ (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb)[‡] were capable of heterogeneously catalyzing the cyanosilylation of aldehydes and ring opening of *meso*-carboxylic anhydrides. No size selectivity for the aldehydes and no enantiomeric excess was however found.[49]



L^1

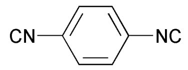


(1)

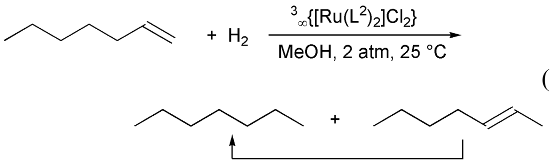
A 3D coordination polymer of Ru(II) with 1,4-diisocyanobenzene ligands (L^2), albeit of not fully known structure, was shown to be a heterogeneous hydrogenation catalyst for 1-hexene. A 3D tetragonal framework of square $[\mathrm{Ru(L^2)_2]Cl_2}$ sheets stacked through Ru–Ru bonds was proposed for the structure. Hydrogenation is accompanied by isomerization, mainly to *trans* 2-hexene, which is only hydrogenated after the consumption of 1-hexene (eqn. (2)). Partial breakage of the Ru–Ru stacking bonds, creating electron-deficient Ru sites and separating the 2D layers on the surface of the particles was invoked for the catalytic mechanism. A related cubic framework $^{3}_{\infty}\{[\mathrm{Ru(L^2)_3]Cl_2}\}$ with bridging 1,4-diisocyanobenzene along all edges (no Ru–Ru bonds) did not exhibit any noteworthy catalytic activity.[50]

[†] The notation $^{n}_{\infty}$[formula] indicates the dimensionality (*n*) of an infinite (∞) framework.

[‡] Ligands are numbered consecutively in their order of graphical appearance as L^1, L^2, L^3, . . . except for the frequently encountered ligands depicted in Fig. 3 and some others which are given by their abbreviation (4,4′-bipy, ox, 1,4-bdc *etc.*). Text drawings are referred to with bold numerals, also in consecutive order (**1**, **2**, **3**, . . .).

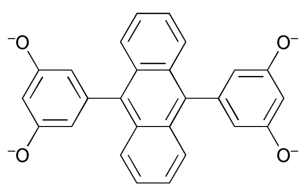


L^2

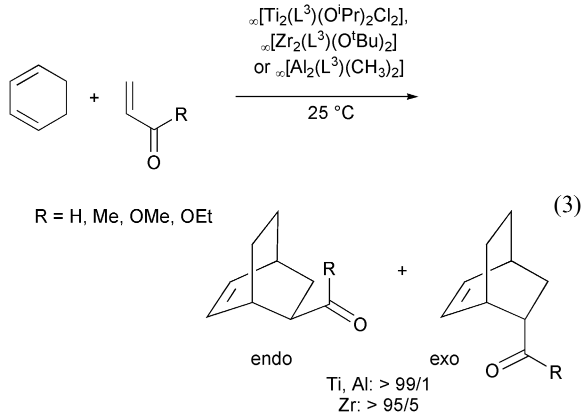


(2)

Lewis-acidic host-networks of formula $[\mathrm{Ti_2(L^3)(O^iPr)_2Cl_2}]$, $[\mathrm{Zr_2(L^3)(O^tBu)_2}]$ or $[\mathrm{Al_2(L^3)(CH_3)_2}]$ but of unknown structures can incorporate and easily desorb various guest molecules, *e.g.* ethyl acetate, ethyl acrylate, acrolein, benzene, 1,3-cyclohexadiene, and catalyze the acrolein or ethylacrylate-1,3-cyclohexadiene Diels–Alder reaction (eqn. (3)). Catalytic activities of the titanium host are said to be much higher than those of its educts, $\mathrm{H_4L^3}$ and $[\mathrm{Ti(O^iPr)_2Cl_2}]$ or $[\mathrm{Zr(O^tBu)_4}]$. The Diels–Alder reaction occurs highly stereoselective with endo/exo typically > 99/1 (Ti, Al) or > 95/5 (Zr).[51,52]

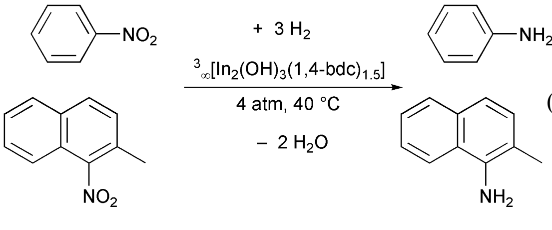


L^3

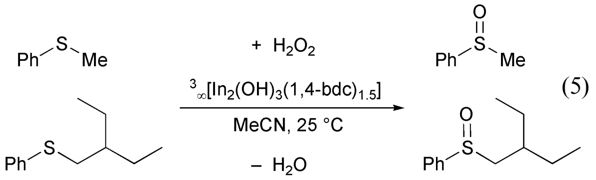


(3)

Also, the capabilities of coordination polymers with no or little porosity are tested in catalysis. The catalytic reactions are thus taking place on the surface. The non-porous polymer $^3_\infty[\mathrm{In_2(OH)_3(1,4\text{-}bdc)_{1.5}}]$ was found active for the hydrogenation of nitroaromatics (eqn. (4)) and the oxidation of alkylphenylsulfides (eqn. (5)). In these surface catalytic reactions the respective reactions rates are quite similar, not showing any dependence on the volume of the substrate. The supernatent liquid phase was proven inactive and did neither show the presence of In metal nor the bdc anion.[53]

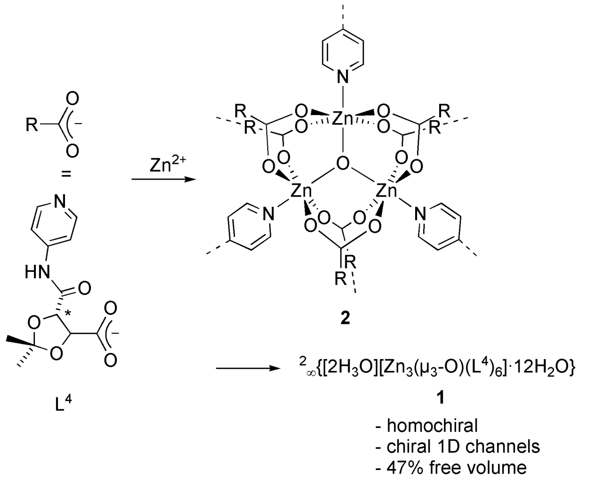


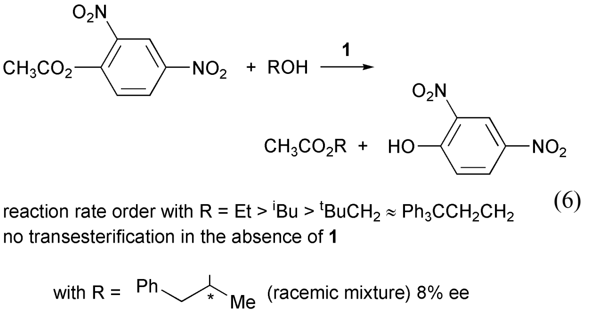
(4)



(5)

The chiral ligand L^4 reacts with zinc ions to a homochiral, open 2D-network of formula $^2_\infty\{[\mathrm{2H_3O}][\mathrm{Zn_3(\mu_3\text{-}O)(L^4)_6}]\cdot 12\mathrm{H_2O}\}$ (**1**).‡ The trinuclear formula unit $[\mathrm{Zn_3(\mu_3\text{-}O)(L^4)_6}]^{2-}$ is sketched in **2**. These building blocks are connected with each other *via* the pyridyl groups of the ligands to form the coordination polymer **1**. However, only three of the six pyridyl groups of the trinuclear unit are needed for the crosslinking. The remaining three pyridyl rings reach into the chiral 1D channels. There, they can serve as anchor groups for substrate molecules. The channels have the form of equilateral triangles with edge lengths of about 13 Å. The channel volume is approximately 47% of the total volume. The porous structure is stable in the presence of solvents. The trans-esterification reaction in eqn. (6) can be carried out in the presence of **1** with a size selectivity. This suggests that the reaction takes place mainly within the channels. The use of sterically demanding alcohols in eqn. (6) lowers the productivity. With a racemic mixture of a chiral alcohol (1-phenyl-2-propanol) a slight enantiomeric excess (8% ee) was observed in the product ester. While such enantiomeric excesses are still small, it is decisive to note this first report of an asymmetric induction in a coordination polymer.[54]





(6)

Titanium aryldioxide coordination polymers of one- to three-dimensionality, $^n_\infty[\mathrm{Ti(OArO)_2(py)_2}]$ (Ar = *p*-$\mathrm{C_6H_4}$-, 2,7-naphthyl, 4,4′-biphenyl; py = pyridine and 4-Me- or 4-Ph-pyridine) were assessed for their Ziegler–Natta polymerization activity towards ethene or propene with methylalumoxane (MAO) as cocatalyst. Polymerization activities were mediocre to poor for ethene and very poor for propene. Fragmentation of the coordination polymer lattice was likely.[55]

Supposedly 3D coordination polymer networks of undetermined structure have been formed in dmso as "metallogels" from $[\mathrm{Pd(en)(H_2O)_2}](\mathrm{NO_3})_2$ or $[\mathrm{Pd(OAc)_2}]$ and multitopic ligands with three to four pendant pyridyl donors (dmso =

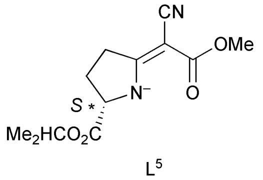
dimethylsulfoxide, en = ethylenediamine, OAc = acetate). Once formed these metallogels were no longer soluble in dmso or other organic solvents (*e.g.* toluene, hexane, thf, CH_2Cl_2) even at elevated temperature (>100 °C). These coordination polymer gels were used as stable catalysts for the oxidation of benzyl alcohol by air into benzaldehyde and a doubled activity of a metallogel over $[Pd(OAc)_2]$ was possible.[56]

Chirality

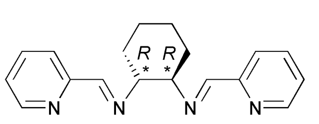
With chirality being an element of life there is also a great interest in the formation of chiral coordination polymers. It is expected that chiral supramolecular architectures could play a role in optical devices. Chiral mircoporous materials are envisioned for enantiomer separation or chiral synthesis.[57] Examples for enantiomer separation using porous chiral frameworks are described under *Porosity*, *zeolite behavior*.[54,58] First uses of chiral porous networks are also described in the section *Catalysis*.[54] In particular for coordination polymers the interest is focused on the preparation of helices with homochirality. The formation of helicoidal chains in one-dimensional coordination polymers is not unusual, with a 2_1-helix (or zig-zag chain) being the most common type. Yet, most helices are formed from achiral ligands which almost always leads to racemic mixtures of *P*- and *M*- (right/left-handed) helices.[28,33,59–61] Of interest are structures which spontaneously resolve to contain only one type of helix, so that chirality is present.

Examples of chiral, non-racemic helical coordination polymers have been reported where the chirality is induced by a stereogenic center of an enantiomerically pure ligand. This can generate either pairs of diastereomeric 2_1-*P*/*M*-polymer strands in the unit cell, as in *P*/*M*-${}^{1}_{\infty}\{[Cu(L^5)_2]$[62] or even a single helix-enantiomer with a sufficient homochiral helicating element in the ligand: The Schiff base L^6 reacts with silver(I) nitrate to produce single-stranded homochiral 2_1-helices ${}^{1}_{\infty}\{[Ag(L^6)]NO_3\cdot 2H_2O\}$ which are arranged in layers perpendicular to a 6_5 screw axis which relates adjacent layers to an overall structure of *M* helicity. Each tetrahedral silver ion in the helix has the *S* configuration.[63] The CHIRAGEN-ligand L^7 together with Ag(I) enabled the enantioselective formation of a *P*-chiral 6_2-double helix, ${}^{1}_{\infty}\{[Ag(L^7)]PF_6\}$. The absolute configuration of the pinene units in the ligand determines the Λ (homo-)chirality of the distorted tetrahedral metal centers and, thus, the chirality of the final structure.[64] The ligand *R*,*R*-DIOP L^8 gave ${}^{1}_{\infty}\{[Ag(L^8)]NO_3\}$ as *P*-chiral 2_1-helices.[65]

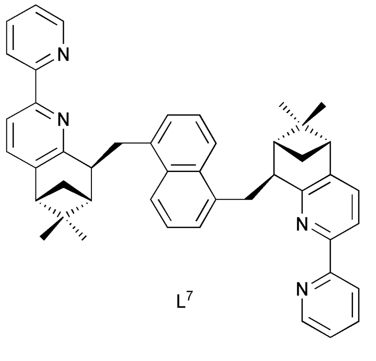
Reaction of racemic Δ/Λ-$[Co^{III}(NH_2CH_2CH_2S)(en)_2]^{2+}$ (en = ethylenediamine) with $AgNO_3$ gives thiolate bridged ${}^{1}_{\infty}\{[Ag\{Co(NH_2CH_2CH_2S)(en)_2\}](NO_3)_2\}$ chains with the chain structure discriminating the chiral Δ or Λ configuration of the cobalt complex to give exclusively the enantiomeric Δ or Λ chains which spontaneously separate from one another as homochiral crystals.[66] The Δ_L-diastereomer of $[Co^{III}$(L-cysteinato-*N*,*S*)$(en)_2]^+$ with $AgNO_3$ leads to ${}^{1}_{\infty}\{[Ag\{Co$(L-cysteinato-*N*,*S*)$(en)_2\}](NO_3)_2\}$ chains which form a left (*M*)-handed helical structure around the crystallographic 3_2 screw axis [cysteinato = $H_2NCH(COO^-)CH_2S^-$]. The Λ_L-diastereomeric cobalt complex yields a 2D sheetlike structure.[67]



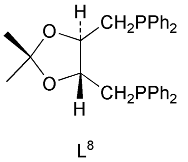
L^5



L^6

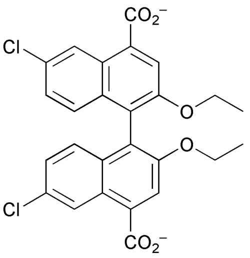


L^7

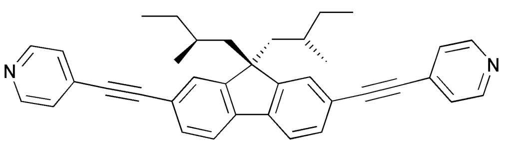


L^8

From the enantiopure ligand L^9 homochiral 2D metal-carboxylate networks of formula ${}^{2}_{\infty}\{[M_2(L^9)_2(\mu\text{-}H_2O)(py)_3(dmf)]\cdot dmf\cdot xH_2O\}$ (M = Mn, Co, Ni)[68] and ${}^{3}_{\infty}\{[Ln_2(L^9)_3(py)_2(def)_2]\cdot 2def\cdot 5H_2O\}$ (Ln = Gd, Er, Sm)[69] were obtained (py = pyridine, dmf = dimethylformamide, def = diethylformamide). Similarly L^{10} gave ${}^{2}_{\infty}\{[Cu(L^{10})_2(NO_3)_2]\cdot CH_2Cl_2\cdot 2EtOH\}$.[70] Enantiomeric forms of the 2D and 3D oxalate-bridged polymers ${}^{2}_{\infty}\{[NBu_4][Mn_\Lambda Cr_\Delta(ox)_3]\}/{}^{2}_{\infty}\{[NBu_4][Mn_\Delta Cr_\Lambda(ox)_3]\}$ and ${}^{2}_{\infty}\{[M_\Lambda(2,2'\text{-bipy})_3][M'_\Lambda M''_\Lambda(ox)_3]\}/{}^{2}_{\infty}\{[M_\Delta(2,2'\text{-bipy})_3]\text{-}[M'_\Delta M''_\Delta(ox)_3]\}$ (M = Ni, Ru, M′M″ = LiCr, M′M″ = Mn_2) were synthesized enantioselectively from resolved $[Cr_{\Lambda/\Delta}(ox)_3]^{3-}$ and $[M_{\Lambda/\Delta}(2,2'\text{-bipy})_3]^{2+}$ (M = Ni, Ru). Solid-state circular dichroism measurements demonstrated the enantiomeric (and optical active) character.[71]

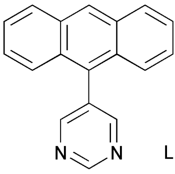


L^9

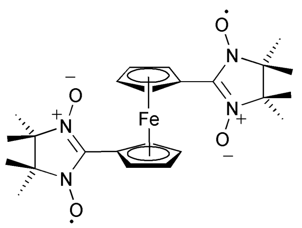


L^{10}

Particularly intriguing is, of course, the formation of a homochiral (helical) coordination polymer from achiral components through spontaneous enantiomer resolution. Such a homochiral helix winding together with homochiral crystallization was reported for the adduct of 5-(9-anthracenyl)pyrimidine (L^{11}) with $Cd(NO_3)_2\cdot H_2O\cdot EtOH$. The chirality arises from a pyrimidine-Cd^{2+} helical array and is preserved in each crystal *via* homochiral interstrand water-nitrate hydrogen bonding. All the crystals are of the same chirality as a result of single-colony homochiral crystal growth (homochiral crystallization).[72] The achiral building blocks in ${}^{1}_{\infty}\{[Ni(PhCOO)_2(4,4'\text{-bipy})]\cdot 2MeOH\}$ give rise to a 4_1 or 4_3-helical polymer with homochirality in the crystal. Different crystals contain statistically either *P*- or *M*-helices.[73] Homochiral right-handed (*P*) 6_1 helices of $Cd\{B(OMe)_4\}$ are found in ${}^{3}_{\infty}\{[Cd(tcm)\{B(OMe)_4\}]\cdot xMeOH\}$ with neighboring helices connected by the tricyanomethanide ion (tcm, see L^{37}).[74] Compound ${}^{1}_{\infty}\{[Mn(hfac)_2(L^{12})]\cdot CH_2Cl_2\}$ spontaneously resolves in enantiomorphous crystals with either Λ or Δ configuration at Mn and additional six sources of chirality within the *P*- or *M*-helices, respectively (hfac = hexafluoroacetylacetonate).[75] Variation of the proton content with KOH/HCl_{aq} allows for a reversible inter-conversion between the achiral molecular square of $[Cu(HL^{13})(H_2O)_{0.5}]_4(ClO_4)_4$ (high pH) and spontaneously resolved homochiral double-chain motif of ${}^{1}_{\infty}\{[H_3O]_2[Cu_3(L^{13})_2Cl](ClO_4)_2(Cl)\}$ (low pH).[76]

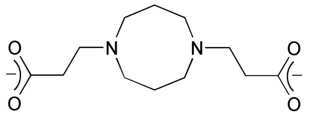


L11



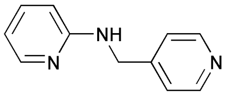
ferrocenyl bis(nitronyl nitroxide)

L12

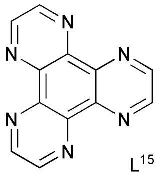


L13

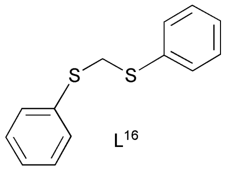
The formation of homochiral 2D and 3D coordination networks within a crystal was reported for ${}^{2}_{\infty}[Ag(L^{76})]$,[77] ${}^{2}_{\infty}\{[Cd_3(\mu_3\text{-}OH)(L^{79})_3(py)_6](ClO_4)_2\}$[78] and ${}^{3}_{\infty}\{[Zn(L^{70})_2]\cdot 0.5H_2O\}$.[79] These frameworks were also proven as NLO materials (see there). Further homochiral crystals were derived from the triangular grid ${}^{2}_{\infty}\{[Cu(PPh_3)(L^{14})_{1.5}]ClO_4\cdot 0.5CHCl_3\}$,[80] the (10,3)-a-nets ${}^{2}_{\infty}\{[Ag(L^{15})]ClO_4\cdot 2MeNO_2\}$ (see also under *Porosity*/Table 4)[81] and ${}^{3}_{\infty}\{[Ag(L^{16})]NO_3\}$[82] and the interpenetrated, quintuble-layered network ${}^{2}_{\infty}\{[Co_5(SO_4)_4(L^{17})(H_2O)_8]SO_4\cdot 14H_2O\}$.[83] From 1,2-bi(4-pyridyl)ethine, L[18] and copper(II) a threefold-interpenetrated chiral network ${}^{3}_{\infty}\{[\{Cu(L^{18})_2(H_2O)_2\}\{Cu(NO_3)_2(L^{18})_2(H_2O)_2\}_2]\text{-}(NO_3)_4\cdot L^{18}\cdot 1.33H_2O\}$ has been obtained.[84]



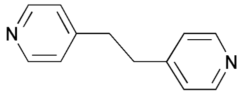
L14



L15

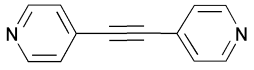


L16



1,2-bis(4-pyridyl)ethane

L17



1,2-bis(4-pyridyl)ethine

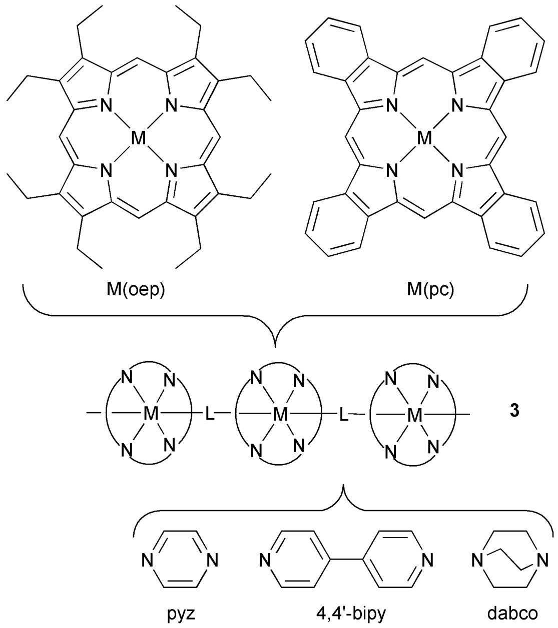
L18

Fourfold and twofold interpenetrated networks, ${}^{2}_{\infty}\{[Ni_3(btc)_2(py)_6(eg)_6]\cdot x eg\cdot y H_2O\}$ ($x \sim 3$, $y \sim 4$) and ${}^{2}_{\infty}\{[Ni_3(btc)_2(py)_6(pd)_3]\cdot x pd\cdot y H_2O\}$ (eg = ethylene glycol, pd = 1,2-propanediol or 1,2-butanediol, $x \sim 11$, $y \sim 8$) can be grown homochiral in a single crystal. The handedness is controlled by hydrogen bonding between btc and the diol ligands bound to the metal center. The diol functions as a template for the chiral phase of the framework. From racemic or nonchiral alcohol templates the single crystals spontaneously resolved to form homochiral helical structures featuring helical networks of uniquely one hand.[85]

Conductivity

Electrical conductivity of polymers continues to be one of the most important research areas in materials science.[86] Conductivity is not the prime focus of research in coordination polymers as short inorganic bridges are required for a good conductivity in extended metal-ligand structures.[45] As a reference point, the conductivity of metals is 10^4–10^5 S cm^{-1} at room temperature and increases with decreasing temperature (1 S = 1 Ω^{-1}).[87]

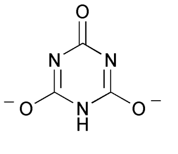
One-dimensional coordination polymers constructed from stacked macrocyclic metal complexes of the type ${}^{1}_{\infty}[M(L)(\mu\text{-}L')]$ (**3**) {with M = Fe, Ru, Os, L = octaethylporphyrinato (oep), phthalocyaninato (pc); L′ = pyz, 4,4′-bipy, dabco} have been examined for their conductivity. Doping with iodine drastically increases their conductivity. The conductivity increases from 1×10^{-6} S cm^{-1} for ${}^{1}_{\infty}[Fe^{II}(pc)(\mu\text{-}pyz)]$ to 2×10^{-1} S cm^{-1} for ${}^{1}_{\infty}[Fe(pc)(\mu\text{-}pyz)I_{2.54}]$. The conductivity of these 1D coordination polymers depends on the interaction of the metal d-orbitals with the π* level of the bridging ligand. Conductivity is greater for better π-bonding metals (Os > Ru > Fe) and for more π-acidic ligands (lower lying π*-orbitals) (pyz > 4,4′-bipy ≫ dabco).[88]



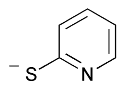
3

Coordination polymers with Ag ··· Ag interactions may possess electrical semiconductive properties. The 3D polymer ${}^{3}_{\infty}[\{Ag(H_2btc)_2\}\{Ag_2(Hbtc)\}]$ with unsupported Ag ··· Ag interactions (2.963–3.278 Å) shows a weak semiconductivity of 1.06×10^{-6} S cm^{-1} (increasing with temperature).[107] The structure of ${}^{3}_{\infty}[Ag_2(L^{19})]$ with 2D sheets of Ag atoms (Ag ··· Ag = 2.95 Å) separated by L[19] has an anisotropic conductivity of *ca.* 5×10^{-3} S cm^{-1} parallel and *ca.* 2×10^{-5} S cm^{-1} perpendicular to the Ag sheets with a static dielectric constant of *ca.* 22 000 at 300 K. The conductivity along the sheets is temperature independent down to 15 K.[108] The silver-pyridine-2-thiolate polymer ${}^{2}_{\infty}[Ag(L^{20})]$ with a graphite-like array of distorted Ag_6 hexagons (Ag ··· Ag 3.215 and 3.250 Å) features an electrical semiconductivity of 2.04×10^{-5} S cm^{-1} at 298 K, increasing with temperature. The pyridine-2-thiolate ligand acts as a μ_3-bridge to link two Ag atoms through the S atom and ligates another silver through an N atom.[109] For comparison, the Ag–Ag distance in metallic silver is 2.89 Å, the van der Waals contact distance is 3.40 Å.[110] The semiconductivity of silver(I) structures is, in turn, seen as evidence for Ag ··· Ag interactions.

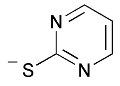
The polymer ${}^{2}_{\infty}[Ni_2(L^{21})_4]$, where each pyrimidine-2-thiolate acts as a μ_3-bridge to link three nickel atoms through the S and N atoms, has a conductivity of 5.00×10^{-3} S cm^{-1} at 28 °C which increases with temperature, indicating a semiconductor.[111] Anisotropic and unusually high—up to—metallic conductivity of 800–1000 S cm^{-1} at 295 K increasing down to 1.3 K up to 500 000 S cm^{-1} was observed for single crystals in the copper(I) compound with the radical anion of a dicyanoquinodiimine L[22], ${}^{2}_{\infty}[Cu(L^{22})_2]$ (powder conductivity was 0.4 S cm^{-1}).[112] Coordination polymeric phases of the μ_4-tetracyanoquinodimethane radical anion, L[23] with Cu(I) can be



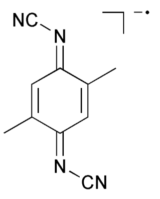
dianion of cyanuric acid
L^{19}



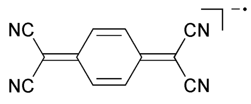
L^{20}



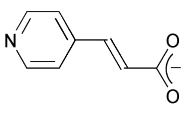
L^{21}



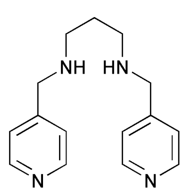
L^{22}



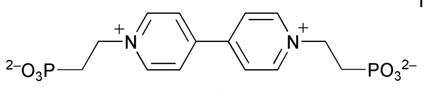
tcnq$^{-\cdot}$
L^{23}



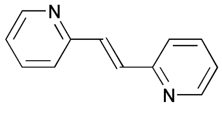
trans-3-(4-pyridyl)acrylate
L^{24}



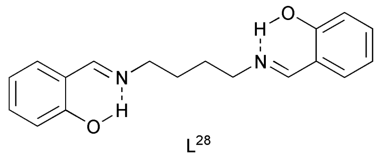
L^{26}



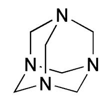
L^{25}



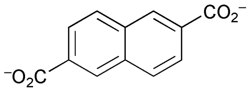
1,2'-bis(2-pyridyl)ethene
L^{27}



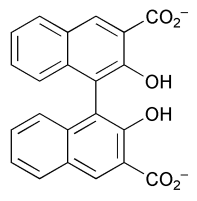
L^{28}



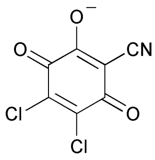
hexamethylenetetramine
L^{29}



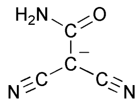
2,6-naphthalenedicarboxylate
L^{30}



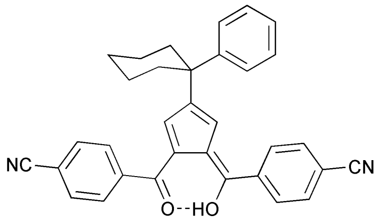
L^{31}



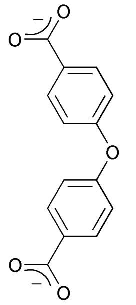
L^{32}



L^{34}



L^{33}



4,4'-oxybis(benzoate)
L^{35}

semiconductors with a room temperature conductivity of up to 0.25 S cm^{-1} and a band gap of down to 0.137 eV.[113]

Luminescence

Coordination polymers are studied for luminescence properties owing to their higher thermal stability than the pure organic ligand and the ability of affecting the emission wavelength of the organic material by metal coordination. The combination of organic spacers and transition-metal centers in coordination polymers is seen as an efficient method for obtaining new types of electroluminescent materials for potential applications as light-emitting diodes (LEDs).[114] Table 1 lists examples of coordination polymers for which luminescence measurements have been reported. The luminescence has been observed in the solid state and at room temperature, unless noted otherwise.

The bathochromic shift of the dabco-compound ${}^3_\infty[Cd_3(btc)_2(dabco)(H_2O)_2]$ compared to the related cadmium–benzene–tricarboxylate complexes ${}^2_\infty[Cd_3(btc)_2(H_2O)_{12}]$, and ${}^3_\infty[Cd_3(Hbtc)_3(H_2O)_8]$ is suggested to be due to σ-donations from the coordination of the amine ligand. This complex also exhibits a quenching of the fluorescence with $\tau = 3.35$ ns.[98]

When the luminescence is due to metal-ligand complex formation it is typically assigned to a ligand-to-metal charge transfer (LMCT) band. Only in few of the above studies it may be deduced that the luminescence could be a specific property of the coordination polymer and as such would differ from the luminescence behavior of related molecular complexes. An example may be ${}^3_\infty[Cd(1,4\text{-bdc})(py)]$ where complex formation significantly (about 100 times) enhances the fluorescent intensity of the free 1,4-bdc ligand, probably due to the symmetry decrease by serious ligand twisting.[100] Such a ligand twisting may indeed be brought upon by the 3D coordination polymer. Also, the room temperature (RT) observation of luminescence in Ag(I) complexes may be a coordination polymeric feature as such examples at RT are scarce.[94,97] Ag(I) complexes are better known to emit luminescence at low temperature.[115] Although, the noted similar luminescence of ${}^2_\infty\{[Ag_3(L^{26})_2](ClO_4)_3\cdot 0.5\,MeCN)\}$ in both the solid state and in acetonitrile solution ($\lambda_{exc} = 290$, $\lambda_{emiss,max} = 390$ nm) argues against a role of the coordination polymer even if the similarity is taken as a (highly doubtful) indication that the polymeric structure might be maintained in solution.[93] Also, compound ${}^3_\infty\{[Ag_2(L^{28})_3](X)_2]$ (X = NO_2, ClO_4) displays fluorescence in acetonitrile solution ($\lambda_{emiss,max} = 460$ nm) which is virtually identical to the solid state (Table 1).[95] To the contrary, the solution, from which the terbium compounds ${}^1_\infty[Tb(O_2CPh)_3(MeOH)_2(H_2O)]$ and ${}^3_\infty[Tb_2(O_2CPh)_6(4,4'\text{-bipy})]$ are grown, already emits bright green fluorescence, attributed to the presence of molecular metal-ligand species. Both benzoate and 4,4′-bipy function as activators and substantially enhance the lanthanoid luminescence intensity from f ⟶ f emission.[104] Also, many gold(I) complexes exhibit luminescence.[116]

In some studies it is made clear, however, that the luminescence is due to the ligand. This is the case for the 2D coordination polymer of europium(III) with carbamyldicyanomethanide (L^{34}), ${}^2_\infty\{[Eu(L^{34})_3(H_2O)_3]\cdot H_2O\}$ for which the fluorescence emission is similar to that of the sodium salt, NaL^{34}, hence, arises from L^{34}.[103]

In the series of the Tb(III) compounds with L^{35} the emission spectra are identical except for their intensity which are in the order ${}^3_\infty\{[Tb_2(L^{35})_3(2,2'\text{-bipy})_2] \gg {}^2_\infty\{[Tb(L^{35})(HL^{35})(H_2O)_2]\cdot H_2O\} > {}^2_\infty[Tb_2(L^{35})_3(H_2O)_4]$ and seen as increasing with the aromatic ring : metal ratio. Luminescence life times were 1.05, 0.82 and 0.79 ms, respectively.[105]

Magnetism

Magnetic studies of coordination polymers are embedded in the area of molecular magnetism and the design of light-weight molecular-based magnets.[45,117] Antiferromagnetism, ferrimagnetism and ferromagnetism are cooperative phenomena of the magnetic spins within a solid. Cooperative magnetic phenomena require that there is an interaction (coupling) between the spins of the paramagnetic centers. In a paramagnet the spin carriers are magnetically isolated. The spin–spin interaction leads to an ordering of the spins below a characteristic, critical temperature (T_c). The goal is a molecular material with a resi-

Table 1 Luminescence studies

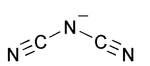
Compound[a]	λ_{exc}/nm	$\lambda_{emiss,max}$/nm	Color	Comment, assignment[b]	Ref.
$^{3}_{\infty}$[Co(2-H$_2$N-1,4-bdc)(L^{17})]	300	400		Strong lum., LMCT	89
$^{3}_{\infty}$[Co(1,4-bdc)(L^{17})]	310	400		Strong lum., LMCT	89
$^{2}_{\infty}${[Cu(PPh$_3$)(L^{14})$_{1.5}$]ClO$_4$·0.5CHCl$_3$}	358	490	Blue	Intraligand π–π*, stronger than in free L^{14}	80
$^{3}_{\infty}$[Zn$_8$(SiO$_4$)(1,3- or 1,4-bdc)$_6$]	315	386 (1,4-bdc)		Stronger than in free bdc, LMCT	
		364 (1,3-bdc)			
	also 338	506 (1,4-dbc)	Green	Lifetime 6.78 ms	90
$^{3}_{\infty}${[Zn(L^{24})$_2$]·*trans*-2-butene}	395	430	Blue	Strong; bathochromic shift *vs.* HL^{24}	91
$^{3}_{\infty}${[Zr(L^{25})]X$_2$} (X = Cl, Br, I)	285	340		Lifetimes < 20 ns	92
$^{3}_{\infty}$[{Ag(H$_2$btc)$_2$}{Ag$_2$(Hbtc)}]	360	460	Blue	Strong lum., LMCT	107
$^{2}_{\infty}${[Ag$_3$(L^{26})$_2$](ClO$_4$)$_3$·0.5MeCN)}	310	398			93
$^{2}_{\infty}${[Ag$_8$(μ$_4$-SO$_4$)$_4$(L^{27})$_5$]·10H$_2$O}	325	398,420,443 (low temperature)			
		~415 (RT)	Blue		94
$^{2}_{\infty}${[Ag$_2$(NO$_2$)$_2$(L^{27})$_3$]	325	422	Blue		94
$^{3}_{\infty}${[Ag$_2$(L^{28})$_3$](X)$_2$] (X = NO$_2$, ClO$_4$)	370	497	Blue	Strong lum.	95
$^{3}_{\infty}${[Ag$_4$(μ$_4$-L^{29})(μ$_4$-L^{30})$_2$]·2H$_2$O}	312	439	Blue	Strong lum.	96
$^{3}_{\infty}${[Ag$_2$(μ-L^{29})$_2$(μ-L^{31})$_2$]·2H$_2$O·MeCN}	334	508			96
$^{3}_{\infty}$[Ag(L^{32})(MeCN)]	350	394	Blue	LMCT	97
$^{2}_{\infty}${[Ag$_2$(SO$_3$CF$_3$)$_2$(L^{33})(H$_2$O)$_2$]·0.5C$_6$H$_6$}		577		Blue-shift from L^{33} lum.	114
$^{2}_{\infty}$[Cd$_3$(btc)$_2$(H$_2$O)$_{12}$]	220	355		Strong lum., LMCT	98
$^{2}_{\infty}$[Cd(ino)$_2$(L^{17})$_{0.5}$(H$_2$O)]	314	509	Blue	Intense, LMCT	99
$^{3}_{\infty}$[Cd$_3$(btc)$_2$(dabco)(H$_2$O)$_2$]	365	437		Strong lum., LMCT	98
$^{3}_{\infty}$[Cd$_3$(Hbtc)$_3$(H$_2$O)$_8$]	218	353		Strong lum., LMCT	98
$^{3}_{\infty}$[Cd(1,4-bdc)(py)]	390	464	Blue	Strong lum., intraligand	100
$^{3}_{\infty}${[Ph$_3$PCH$_2$Ph][Cd(bdc)Cl]·2H$_2$O}	292	474		Strong lum., LMCT	101
$^{1}_{\infty}${[Au(Ph$_2$PCH=CHPPh$_2$)$_{1.5}$](CF$_3$CO$_2$)·MeOH} and			Blue-	Strong lum., Au centered	102
$^{2}_{\infty}${[Au(Ph$_2$P(CH$_2$)$_3$PPh$_2$)$_{1.5}$][Au(CN)$_2$]·2MeOH}					
		420 (br)	Purple	$a_2''(6p_z) \longrightarrow e'(d_{x^2-y}, d_{xy})$ with π*(Ph) contrib.	
$^{2}_{\infty}${[Eu(L^{34})$_3$(H$_2$O)$_3$]·H$_2$O}	484	660		Intraligand lum. from L^{4L}	103
$^{1}_{\infty}$[Tb(O$_2$CPh)$_3$(MeOH)$_2$(H$_2$O)]	300,368	(490) 545	Green	$(^5D_4 \longrightarrow {}^7F_6)$ $^5D_4 \longrightarrow {}^7F_5$	104
		(587,624)		$(^5D_4 \longrightarrow {}^7F_4, {}^5D_4 \longrightarrow {}^7F_3)$	
$^{3}_{\infty}$[Tb$_2$(O$_2$CPh)$_6$(4,4′-bipy)]	300	(490) 545	Green	$(^5D_4 \longrightarrow {}^7F_6)$ $^5D_4 \longrightarrow {}^7F_5$	104
		(587,624)		$(^5D_4 \longrightarrow {}^7F_4, {}^5D_4 \longrightarrow {}^7F_3)$	
$^{2}_{\infty}${[Tb(L^{35})(HL^{35})(H$_2$O$_2$)]·H$_2$O}	308	490,545,585,625		$^5D_4 \longrightarrow {}^7F_n$, $n = 6,5,4,3$	105
$^{2}_{\infty}$[Tb$_2$(L^{35})$_3$(H$_2$O)$_4$]	308	490,545,585,625		$^5D_4 \longrightarrow {}^7F_n$, $n = 6,5,4,3$	105
$^{3}_{\infty}${[Tb$_2$(L^{35})(2,2′-bipy)$_2$]	308	490,545,585,625		$^5D_4 \longrightarrow {}^7F_n$, $n = 6,5,4,3$	105
$^{3}_{\infty}${[Tb$_2$(1,4-bdc)$_3$(H$_2$O)$_2$]·2H$_2$O} $^{3}_{\infty}${[Tb$_2$(1,4-bdc)$_3$]} $^{3}_{\infty}${[Tb$_2$(1,4-bdc)$_3$(NH$_3$)$_2$]·2NH$_3$}	254	~490,545,585,625		$^5D_4 \longrightarrow {}^7F_n$, $n = 6,5,4,3$ decay const.: $k_{obs} = 1.13 \pm 0.02$ ms^{-1} $k_{obs} = 0.74 \pm 0.01$ ms^{-1} $k_{obs} = 1.00 \pm 0.01$ ms^{-1}	106

[a] Arbitrarily ordered by mass of metal atom. For btc, 1,3-bdc, 1,4-bdc, dabco and ino see Fig. 3; py = pyridine, 2,2′-bipy = 2,2′-bipyridine. [b] LMCT = ligand to metal charge transfer.

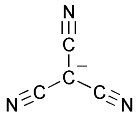
dual permanent magnetization at zero-field for an as high as possible T_c. This requires a structure that allows for parallel coupling of the spins (↑↑↑↑, ferromagnetism) or the antiparallel coupling of unequal spins (↑↓↑↓, ferrimagnetism) of neighboring paramagnetic spin carriers so that a non-zero spin of the bulk material results. In addition there are canted spin orientations.[118] There is a propensity for antiparallel coupling of spins (↑↓↑↓, antiferromagnetism) as the state of low-spin multiplicity is often more stable than the state of high-spin multiplicity.

In molecular materials the spin carriers are paramagnetic metal centers or organic radicals. When the spin centers are not directly adjacent their exchange interactions have to be transmitted by the connecting diamagnetic ligands. It is important to note that ferromagnetism is a three-dimensional property. While the spin exchange interactions in molecular magnets may be large in one or two dimensions, they are usually weak in the remaining dimensions. Thus, T_c of these low-dimensional compounds is typically below 10 K. To increase T_c, strong interactions in all three dimensions are needed. For ferromagnetic coupling the magnetic orbitals of adjacent centers have to be orthogonal.

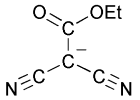
Multitopic, closed shell organic ligands which are typically used in coordination polymers give mostly rise to only weak magnetic interactions. In order to achieve a strong coupling between the metal centers with their unpaired electrons, short oxo, cyano or azido bridges are needed. Polymeric metal cyanide compounds are frequently encountered in magnetic investigations.[119,120] However, these metal-cyanide polymers, built from "inorganic" bridging ligands, are outside the scope of this article. The ligands dicyanamide [dca, $\mathrm{N(CN)_2^-}$, $\mathrm{L^{36}}$] or tricyanomethanide [tcm, $\mathrm{C(CN)_3^-}$, $\mathrm{L^{37}}$] also lead to homoleptic and heteroleptic extended lattices of the general formulae $\mathrm{M(dca)_2}$, M(dca)(tcm) and $\mathrm{M(tcm)_2}$[121] which show long-range magnetic ordering through M–NCN–M exchange pathways when tridentate dca is present.[122] End-to-end bridging dca[123] or tcm[124] have a low efficiency to mediate electronic interactions ($J < -0.4\ \mathrm{cm^{-1}}$ for dca). The related polynitrile ligands $\mathrm{L^{38}}$ or $\mathrm{L^{39}}$ give rise to only very weak antiferromagnetic coupling when bridging between metal centers, *e.g.* in $^{1}_{\infty}[\mathrm{M^{II}(L^{38})_2(H_2O)_2}]$ (M = Mn, Fe, Co, Ni, Cu)[125] or $^{3}_{\infty}[\mathrm{Cu^{II}(L^{39})(H_2O)_2}]$.[126] $^{2}_{\infty}[\mathrm{Cu^{II}}$-$\mathrm{(L^{39})(en)_2}]$ is a paramagnet.[127] The tetracyanoethenide radial anion, $\mathrm{tcne^{-\bullet}}$ ($\mathrm{L^{40}}$) can bridge between two or four metal sites as in $^{1}_{\infty}[\mathrm{Mn^{III}(porphyrin)(\mu\text{-}tcne^{-\bullet})}]$ or $^{3}_{\infty}[\mathrm{M^{II}(\mu_4\text{-}tcne^{-\bullet})_2}]$ (M = V, Mn, Fe, Co, Ni) and result to several classes of "organic" magnets[128,129] with $\mathrm{V(tcne)}_x\cdot y\mathrm{CH_2Cl_2}$ ($x \sim 2$, $y \sim 0.5$) being a room-temperature magnet.[130]



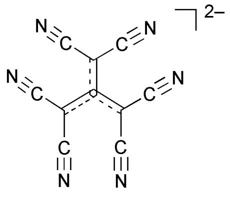
dicyanamide, dca
$\mathrm{L^{36}}$



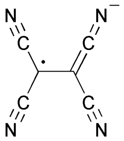
tricyanomethanide, tcm
$\mathrm{L^{37}}$



$\mathrm{L^{38}}$

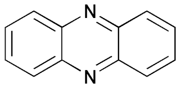


$\mathrm{L^{39}}$

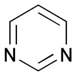


tetracyanoethylenide, $\mathrm{tcne^{-\bullet}}$
$\mathrm{L^{40}}$

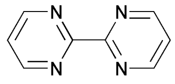
Bridging coligands like 4,4′-bipyridine (4,4′-bipy), pyrazine (pyz), phenazine ($\mathrm{L^{41}}$), pyrimidine ($\mathrm{L^{42}}$) *etc.* may be present in metal-cyanide, -azide,[131] halide[132] or -dicyanamide[133–135] networks (see also below). The pathways through the coligands usually transmit a very weak antiferromagnetic behavior, except for 2,2′-bipyrimidine ($\mathrm{L^{43}}$).[136] Also, in $^{3}_{\infty}[\mathrm{Mn(\mu\text{-}dca)_2(\mu\text{-}pyz)}]$ the exchange interaction is much stronger along the Mn–pyz–Mn chain axis than along the Mn–dca–Mn axes by a factor of about 40.[137] Compounds $^{2}_{\infty}[\mathrm{M^{II}(\mu\text{-}N_3)_2(\mu\text{-}pyz)}]$ form a 2D planar layer-structure by the μ-1,1′-bridging action of the azide and the pyrazine ligand. The azide-bridged linear chains of $\{\mathrm{M(\mu\text{-}N_3)_2}\}_{\infty}$ contain ferromagnetically coupled metal atoms with $J/k = 6.1$ K ($J = 4.2\ \mathrm{cm^{-1}}$) for M = Fe[138] and $J/k = 0.61$ K ($J = 0.42\ \mathrm{cm^{-1}}$) for M = Mn[139] ($k$ = Boltzmann constant 0.695 $\mathrm{K^{-1}\ cm^{-1}}$). At the same time the metal atoms exhibit an antiferromagnetic interaction through the pyrazine bridges ($zJ'/k = -1.19$ K and -0.48 K, respectively with $z = 2$). The iron compound has been described as metamagnetic because of these alternating and competitive magnetic couplings.[138] In the layer structures $^{2}_{\infty}[\mathrm{Co(NCS)_2(\mu\text{-}pyz)_2}]$ and $^{2}_{\infty}[\mathrm{Co(NCS)_2(\mu\text{-}L^{42})_2}]$ the pyrazine network displays antiferro-, the latter pyrimidine network ferromagnetic interactions at low temperature (terminal NCS-ligands in both cases).[140]



phenazine
$\mathrm{L^{41}}$

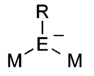


pyrimidine
$\mathrm{L^{42}}$



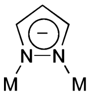
2,2'-bipyrimidine
$\mathrm{L^{43}}$

Stronger coupling mediated by closed-shell organic ligands requires either a single-atom (**4**) or a conjugated two- to three-atom bridge as with pyrazolate (**5**),[141] 1,2,4-triazole/triazolate (**6**/**7**)[142] or carboxylate (**8**) between the metal centers (see below). The related imidazolate (imi) bridge (**9**) is known to induce moderate antiferromagnetic[143] and also ferromagnetic coupling.[144] The oxalate dianion $\mathrm{C_2O_4^{2-}}$ (ox) is widely used as a bridging ligand to enable strong magnetic interactions between paramagnetic centers when adopting the bisbidentate coordination mode (**10**). The oxalate dianion has allowed the isolation of heterometallic 2D and 3D magnetic networks (**11**, *e.g.* $[\mathrm{Mn^{II}Cr^{III}(ox)_3}]^-$) which exhibit ferro-,[145,146] ferri-,[147] or canted antiferromagnetic[148] long-range ordering.[149] In general, layered structures containing $^{2}_{\infty}[\mathrm{M^{II}M^{III}(ox)_3}]^-$ units are obtained when $[\mathrm{ER_4}]^+$ (E = N, P; R = alkyl group) is used. Whereas 3D networks result when the charge is counterbalanced by tris-chelated $[\mathrm{M(2,2'\text{-}bipy)_3}]^{2/3+}$.[169] The compounds of the $\mathrm{M^{II}Cr^{III}}$ series behave as ferromagnets, while in the $\mathrm{M^{II}Fe^{III}}$ series the coupling is antiferromagnetic giving rise to ferrimagnets (for $\mathrm{M^{II}}$ = Fe, Co) or canted antiferromagnets (for $\mathrm{M^{II}}$ = Mn).[150] The



(E = O , S)

4



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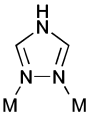

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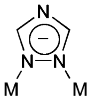

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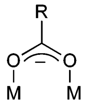

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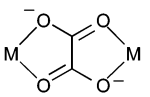

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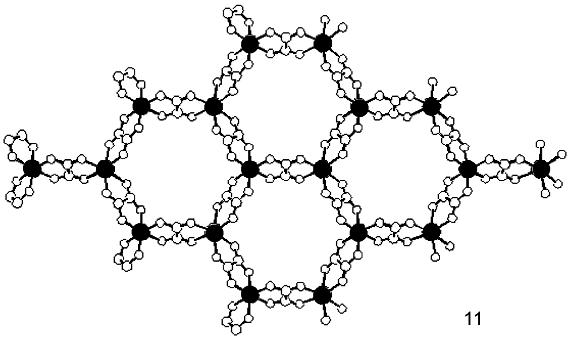
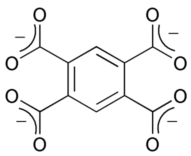
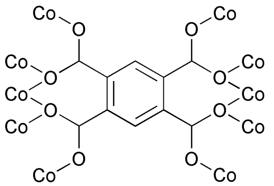


11

mixed-valence complex $^{2}_{\infty}\{[N^{n}Pr_4][Fe^{II}Fe^{III}(C_2O_2S_2)]\}$ with the related dithiooxalato ligand displays ferromagnetic order below ~6 K.[151]

The magnetic behavior of the 3D cobalt(II)-pyromellitate coordination polymer, $^{3}_{\infty}[Co_2(L^{44})]$ is complex with three ground states (collinear and canted antiferromagnetism and field-induced ferromagnetism) but can be traced to the coordination mode of L^{44} which form 12 bonds to 10 metal atoms, including four *O*-bridges (**12**).[152a] Cyclohexane-1,3,5-tricarboxylate (L^{45}) with also a carboxylate group bridging between three metals leads to antiferromagnetic interactions in $^{3}_{\infty}\{[Co_3(L^{45})(\mu\text{-}H_2O)_2(H_2O)_2]\cdot 5H_2O\}$ and mostly ferromagnetic interactions in the nickel analog.[152b] When metal-carboxylate units, $M_x(O_2CR)_y$ are extended into coordination polymers with bridging coligands strong coupling (if at all) is usually observed only within the metal-carboxylate subunit.[153] However, in $^{1}_{\infty}\{[\{Cu(\mu\text{-}OAc)\}_2\{Cu(L^{46})_2\}](ClO_4)_2\cdot 2MeOH\cdot 2H_2O\}$ the three copper(II) atoms are ferromagnetically coupled through the ligand L^{46} (**13**).[154] Use of the ligand 1,3-bdc which bridges between dimetal-tetracarboxylate secondary building units $\{M_2(RCO_2)_4\}$ enhances the interdimer interaction. The intradimer coupling is $J = -350\ cm^{-1}$ and $J = -380\ cm^{-1}$ in $^{2}_{\infty}\{[Cu_2(1,3\text{-}bdc)_2(py)_2]_3\}$ and $^{2}_{\infty}\{[Cu_2(1,3\text{-}bdc)_2(py)_2]_4\}$, respectively, compared to the interdimer coupling of $J = -18\ cm^{-1}$ and $J = -85\ cm^{-1}$.[155]


benzene-1,2,4,5-tetracarboxylate, pyromellitate
L^{44}



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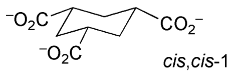
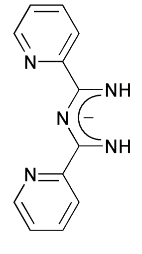
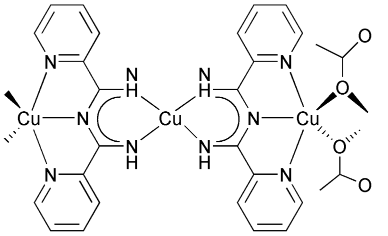


L^{45} *cis,cis*-1,3,5-cyclohexane-tricarboxylate



L^{46}

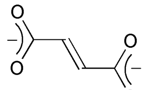


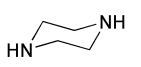
13

Organophosphonate anions, *e.g.* $^{-}HO_3PCH_2PO_3^{2-}$, $^{-2}O_3P\text{-}CH_2PO_3^{2-}$ in their metal coordination polymers mostly give rise to unexceptional magnetic behavior.[156] Short-range antiferromagnetic coupling is observed in $^{3}_{\infty}[V(HO_3PCH_2PO_3)(H_2O)]$,[156] 2D antiferromagnetic behavior below 13 K in $^{2}_{\infty}\{[Fe_2(HO_3PCH_2PO_3)_2(H_2O)_2]\cdot 2H_2O\}$.[157]

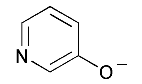
Studies of magnetic behavior in coordination polymers with most of the typical multitopic closed-shell organic ligands can usually be considered routine with unremarkable results.[158] An exception are pyrazole and triazole based coordination polymers. The short N–N bridge provided by these ligands (*cf.* **5**–**7**) effectively transmits electronic interactions.[141,142] Also, the through-bond coupling in Cu(II)-piperazine systems leads to sizable magnetic interactions, *e.g.* in $^{2}_{\infty}\{[Cu(fumarate, L^{47})(L^{48})]\cdot 2H_2O\}$ ($J = -15.3\ cm^{-1}$).[159] The bridging pyridin-3-onato anion L^{49} in $^{1}_{\infty}\{[Cu(\mu\text{-}L^{49})(L^{49})(HL^{49})(H_2O)]\cdot 2H_2O\}$ gives an antiferromagnetic interaction with $J = -16.4\ cm^{-1}$.[160]

An exceptional bridging (co)ligand is also 2,2′-bipyrimidine (L^{43}). Significant to strong antiferromagnetic interactions ($J = -1.2\ cm^{-1}$ [136b,161] to $-211\ cm^{-1}$ [136a]) can be mediated by bis-bidentate 2,2′-bipyrimidine ligands between M^{II} centers (**14**, *cf.* to **10**) in one- and two-dimensional (hybrid) structures with 3d transition metals.[136,161] Examples for antiferromagnetically coupled metal atoms in 1D chains formed by only bridging L^{43} are found in $^{1}_{\infty}[Mn(NCO)_2(L^{43})]$ ($J = -0.78\ cm^{-1}$),[162] in the copper complexes $^{1}_{\infty}\{[Cu(L^{43})(H_2O)_2](ClO_4)_2\cdot H_2O\}$ ($J = -62\ cm^{-1}$),[163] $^{1}_{\infty}\{[Cu(L^{43})(H_2O)_2](NO_3)_2\cdot H_2O\}$ ($J = -55\ cm^{-1}$), $^{2}_{\infty}[Cu(Cr_2O_7)(L^{43})]$ ($J = -147\ cm^{-1}$) and $^{3}_{\infty}\{[Cu(SO_4)(L^{43})]\cdot H_2O\}$ ($J = -39\ cm^{-1}$).[164] In the latter two, the chains are connected through the anions into 2D and 3D polymers, respectively. The bis-bidentate ligand bi-imidazolate dianion (L^{50}), related to L^{43}, was found to yield only a weak ferromagnetic ground state with Fe(II) in the presumably 3D lattice $^{3}_{\infty}[Fe(L^{50})]$.[165] Mixed 2,2′-bipyrimidene(oxalato)metal compounds such as $^{2}_{\infty}[Cu_2(ox)Cl_2(L^{43})]$ exhibit strong antiferromagnetic interaction through both the μ-ox ($J = -189\ cm^{-1}$) and μ-L^{43} bridges ($J = -30\ cm^{-1}$)[166] while $^{2}_{\infty}\{[Cu_2(ox)_2(L^{43})]\cdot 5H_2O\}$,[167] $^{2}_{\infty}\{[Mn_2(ox)_2(L^{43})]\cdot 6H_2O\}$,[168] $^{2}_{\infty}\{[NaCr(ox)_2(L^{43})]\cdot 5H_2O\}$ [169,170] show only weak antiferromagnetic interactions.

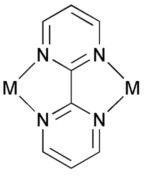

fumarate
L^{47}



piperazine
L^{48}



pyridine-3-onate
L^{49}



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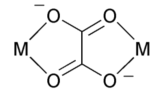

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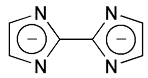
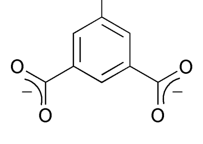
(repeated)

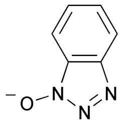


L^{50}

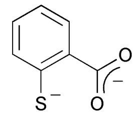
The terephthalate ligand 1,4-bdc has been studied to probe the limiting distance of magnetic exchange between paramagnetic metal centers. In the bis-monodentate mode, 1,4-bdc bridges give typical M ··· M separations of 11 Å. The magnitude of the antiferromagnetic coupling increases with coplanarity of the 1,4-bdc ligand with one of the metal basal planes and can reach from $J = -0.065$ to $-1.6\ cm^{-1}$ in Mn^{II} complexes.[171] In $^{1}_{\infty}\{[Cu(1,4\text{-}bdc)(H_2O)_2]\cdot H_2O\}$ and $^{2}_{\infty}[Cu(1,4\text{-}bdc)(H_2O)_2]$ an antiferromagnetic interactions occurs *via* the 1,4-bdc bridges.[172] Compound $^{3}_{\infty}[Co_2(OH)_2(1,4\text{-}bdc)]$ behaves like a collinear antiferromagnet between 44 and 48 K, and below 44 K a weak spontaneous magnetization or metamagnetic behavior is observed, depending on the applied field.[173] The ligand 5-aminoisophthalate, L^{51} transmits weak antiferromagnetic and ferromagnetic interaction among the metal atoms in $^{2}_{\infty}[Co(L^{51})(H_2O)]$ and $^{1}_{\infty}[Ni(L^{51})(H_2O_2]$, respectively.[174]



5-aminoisophthalate,
L^{51}



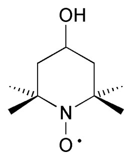
L^{52}

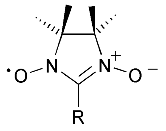


L^{53}

In the one-dimensional coordination polymer $^{1}_{\infty}[Mn_3(L^{52})_2(NCS)_4(DMF)_8]$ an antiferromagnetic coupling originates within the dinuclear $[Mn_2(L^{52})_2(NCS)_2(DMF)_6]$ subunits with $Mn_2(O\text{–}L^{52})_2$ cores which are linked *via* *N*–L^{52} by $Mn(NCS)_2(DMF)_2$ bridges.[175] The diamond-like framework $^{3}_{\infty}[Cu(L^{52})_2(MeOH)]$ is a soft magnet exhibiting two critical temperatures at 6.4 and 4.4 K.[176] The polymer $^{2}_{\infty}[Ni_2(L^{21})_4]$ features ferromagnetic interactions ($J = 19.5\ cm^{-1}$) between the nickel(II) centers of the S-bridged dimer unit and antiferromagnetic interactions ($J = -7.3\ cm^{-1}$) both between adjacent dimer units and between adjacent layers.[111] Compound $^{2}_{\infty}[\mathrm{CoL}^{53}]$ with the thiosalicylate dianion L^{53} displays canted antiferromagnetism with the strong interaction mediated by Co–S–Co bridges.[177]

In the field of molecular-based magnetic materials a *metal-radical approach* has attracted attention in the last few years.[178] The nitroxide ligand L^{54} and $\mathrm{Cu(hfac)_2}$ formed a polymeric chain with alternating ferro and antiferromagnetic exchange (hfac = hexafluoroacetylacetonate).[179] From the combination of metal ions and the nitronyl nitroxide radical (L^{55}) one of the first ferrimagnetic chains, $^{1}_{\infty}[\mathrm{M(hfac)_2(L^{55})}]$ (M = Ni, Mn; R = Me, Et, ^{i}Pr, ^{n}Pr, Ph) with low-temperature magnetic order was designed.[180] $^{1}_{\infty}[\mathrm{Co(hfac)_2(L^{55a})}]$ behaves as an Ising ferrimagnet with slow magnetic relaxation and hystereses effects.[181] The linear chain adducts from $\mathrm{Rh_2(hfac)_4}$ dimers and L^{55} (R = Ph and Me) exhibit fairly large antiferromagnetic interactions ($J = -167$ and $-197\ \mathrm{cm^{-1}}$, respectively).[182] The weakly basic character of nitronyl nitroxides limits their use as a ligand. This led to the synthesis of functionalized nitronyl nitroxide radicals in which a strongly coordinating group is incorporated (L^{55b}–L^{55d}). Using this strategy linear ferrimagnetic chains have been obtained with Mn(II) and $\mathrm{L}^{55b}/\mathrm{HL}^{55b}$ ($J \approx -45\ \mathrm{cm^{-1}}$);[183] two-dimensional Mn(II) nets with ferromagnetic ordering at low temperature were reported with L^{55b} and L^{55c}.[184] Among such functionalized nitronyl nitroxide radicals, the pyridyl-substituted one (L^{55d}) is more widely used to construct extended coordination compounds with varying degrees of magnetic coupling.[185] In $^{1}_{\infty}[\mathrm{Cu_2\{O_2CCMe_3\}_2(L^{55d})}]$ the dinuclear copper-carboylate units are linked *via* the nitrogen atom of the pyridyl ring and the oxygen atom of the NO group to form a chain structure with strong antiferromagnetic interactions between the Cu(II) centers.[186] The two-dimensional structure of $^{2}_{\infty}[\mathrm{Cu(N_3)_2(L^{55d})}]$ is constructed solely through the bridging action of L^{55d} (the azide groups are terminal ligands) and exhibits ferromagnetic interactions.[187]


L54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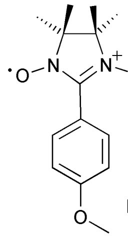
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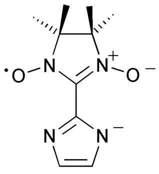
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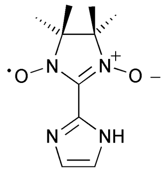
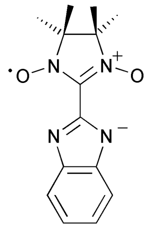

HL55b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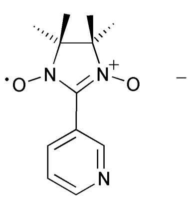
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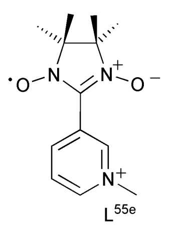
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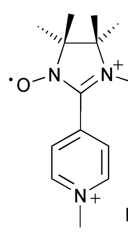
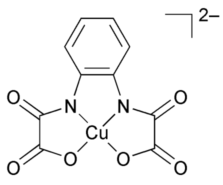
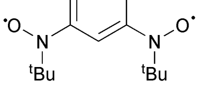
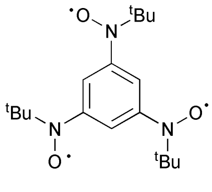
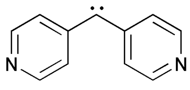

L55f

In the silver(I) complex of L^{55e} of formula $^{1}_{\infty}[\mathrm{Ag(L^{55e})(NO_3)_2}]$ the metal mediates the rather strong ($J/k = -84$ K, $J = -58\ \mathrm{cm^{-1}}$) antiferromagnetic spin–spin interactions of the bridging nitronyl nitroxide ligands.[188] From L^{55f}, Mn(II) and Cu-*o*-phenylenebis(oxamato) (Cu–L^{56}) graphite-like networks are constructed with the corners of each hexagon occupied by Mn ions, the edges formed by L^{56} linking the manganese ions through the oxamato moieties. These networks interpenetrate nearly perpendicular with the nitronyl nitroxide bridging between Cu centers of different nets—this compound of formula $^{2}_{\infty}\{[\mathrm{Mn_2\{(Cu{-}L^{56})_3(L^{55f})_2(dmso)_2\}}]\cdot 2\mathrm{H_2O}\}$ behaves as a magnet below 22.5 K.[189]


Cu-L56


L57


L58


L59

Chains of the diradical L^{57} with Mn(II)(hfac)$_2$ exhibit of ferro- and antiferromagnetic coupling,[190] while a 2D network from L^{58} and Mn(II)(hfac)$_2$ of formula $^{2}_{\infty}\{[\mathrm{Mn_3(hfac)_6(L^{58})_2}]\cdot {}^{n}\mathrm{C_7H_{16}}\}$ yields ferro- and ferrimagnetic ordering.[191] In $^{1}_{\infty}[\mathrm{Mn(hfac)_2(L^{59})}]$ the photochemically generated triplet carbene (from L^{59}–$\mathrm{N_2}$) leads to a ferrimagnetic coupling of the manganese atoms along the chain.[192]

Spin-transition behavior

Spin-transition or spin-crossover is the thermal, light or pressure induced (cooperative) transition between a low-spin (LS) and a high-spin (HS) state. For potential applications the spin-transition should be abrupt due to cooperative phenomena and occur with a thermal hysteresis which confers a memory effect on the system. Room temperature should fall in the middle of the hysteresis loop. Spin-crossover materials could have potential applications, *e.g.* as temperature sensors, as active elements of various types of displays, as optical switches in new electronic devices, and in information storage and retrieval.[193]

The spin-crossover behavior is an example for bistable systems. The spin-equilibrium is best investigated in iron(II) chemistry, to a lesser extent for iron(III) and seldom in cobalt(II).[194–196] The transition from low-spin Fe(II) ($S = 0$, $^{1}\mathrm{A}_1$-state) to high-spin ($S = 2$, $^{5}\mathrm{T}_2$-state) is coupled with a change in magnetic moment, bond length or complex size and a thermochromic effect (purple to white). It is also possible to switch from LS to HS with green and from HS to LS with red light at a temperature where only the LS state is stable (LIESST, light induced excited spin-state trapping).[194] The singlet state is the thermodynamically more stable state. The sharpness of the effect and, in some cases, thermal hysteresis have been linked to strong intermolecular interactions (H-bonds, π–π interactions) or cooperative phenomena which spread the ~10% (0.15 to 0.2 Å) Fe-ligand bond-length distortion over the whole crystal. Sample preparation can markedly effect the cooperativity and consequently hysteresis and HS/LS residual fraction at low and high temperature.

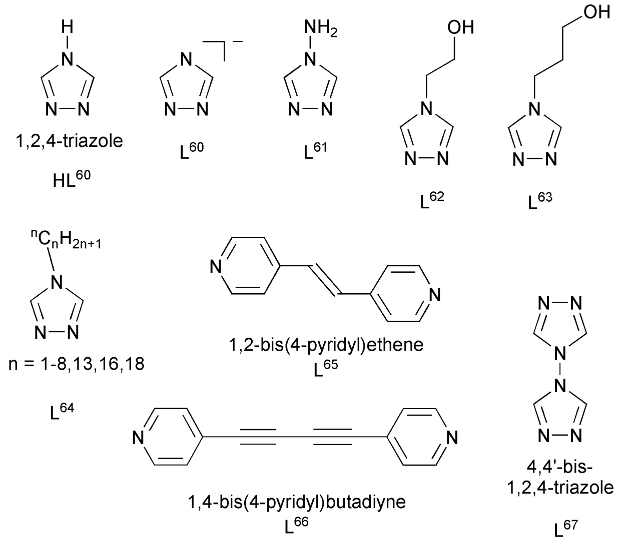
Spin-transition studies are, so far, mostly carried out on mononuclear[197] and occasionally dinclear[198] molecular complexes.[194,195] Only a few polymeric iron(II) spin-crossover compounds have been reported. Yet, one might expect that direct covalent bonding could increase the contact and, hence, the cooperativity between the spin-changing metal centers.[199] Until now, however, polymeric spin-crossover compounds (Table 2) do not seem to present a substantial improvement over molecular counterparts. Methods to follow the high-spin

Table 2 Coordination polymers with spin-crossover behavior

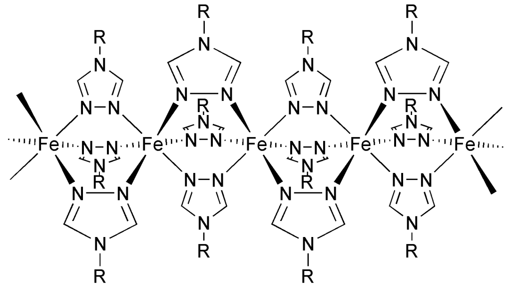
Coordination polymer[a]	Transition temperature (T)[b,c] and comments	Ref.
${}^{1}_{\infty}\{[\mathrm{Fe(HL^{60})_3](ClO_4)_2}\}^{d}$	$T \approx 265$ K (smooth), 5 K hysteresis	202
${}^{1}_{\infty}\{[\mathrm{Fe(HL^{60})_3](ClO_4)_2{\cdot}H_2O}\}^{d}$	$T\downarrow = 304$ K, $T\uparrow = 319$ K (abrupt)	202
${}^{1}_{\infty}\{[\mathrm{Fe(L^{61})_3](ClO_4)_2}\}^{d}$	$T \approx 130$ K (smooth)	202
${}^{1}_{\infty}\{[\mathrm{Fe(L^{61})_3](ClO_4)_2{\cdot}H_2O}\}^{d}$	$T\downarrow = 187$ K, $T\uparrow = 189$ K (abrupt)	202
$[\mathrm{Fe(L^{61})_3]I_2}^{d}$	$T\downarrow = 269$ K, $T\uparrow = 275$ K	203
${}^{1}_{\infty}\{[\mathrm{Fe(L^{61})_3]X_2{\cdot}2H_2O}\}^{d}$ X = naphthalene sulfonate derivatives	$T\uparrow$(LS ⟶ HS) ≈ 330–340 K depending on anion, non-classical transition with loss of $2H_2O$,	204
${}^{1}_{\infty}\{[\mathrm{Fe(L^{61})_3]X_2}\}^{d}$ X = 1-naphthalene sulfonate	T from 229 to 297 K with hysteresis, depending on anion, $T\downarrow = 283$ K, $T\uparrow = 297$ K	204
${}^{1}_{\infty}\{[\mathrm{Fe(L^{61})_3](tosylate)_2{\cdot}2H_2O}\}^{d}$	$T\uparrow$(LS ⟶ HS) = 361 K, non-classical transition with loss of $2H_2O$,	205
${}^{1}_{\infty}\{[\mathrm{Fe(L^{61})_3](tosylate)_2}\}^{d}$	$T\downarrow = 279$ K, $T\uparrow = 296$ K	205
${}^{1}_{\infty}\{[\mathrm{Fe(HL^{60})_{3-3\mathit{n}}(L^{61})_{3\mathit{n}}](ClO_4)_2{\cdot}\mathit{x}H_2O}\}^{d}$	$0 \le n \le 1$: $T\downarrow = (303.0–116.4n)$ K, $T\uparrow = (319.7–129.7n)$ K, $n = 0.15$: $T\downarrow = 285.5$ K, $T\uparrow = 300.2$ K	202
${}^{1}_{\infty}\{[\mathrm{Fe(HL^{60})_3](BF_4)_2{\cdot}H_2O}\}^{d}$	Two phases a—440 K ⟶ b (metastable) a: $T\downarrow = 323(9)$ K, $T\uparrow = 345(13)$ K[c] (abrupt) b: $T\downarrow = 276(7)$ K, $T\uparrow = 282(4)$ K[c] (abrupt)	206
${}^{1}_{\infty}\{[\mathrm{Fe(L^{60})(HL^{60})_2](BF_4)_2{\cdot}H_2O}\}^{d}$	Two modifications a and b a: $T\downarrow = 345(4)$ K, $T\uparrow = 385(4)$ K[c] (abrupt) with increasing hysteresis upon thermal cycles up to $\Delta T\downarrow\uparrow$ 50 K; b: $T\downarrow = 325(20)$ K, $T\uparrow = 370$-$345(4)$ K[c] (less abrupt than a) with decreasing hysteresis (shift of $T\uparrow$) upon thermal cycles	206
${}^{1}_{\infty}\{[\mathrm{Fe(L^{60})_2(HL^{60})]X}\}^{d}$	X = BF_4 $T\downarrow = 341$-351 K, $T\uparrow = 371$-385 K, various samples	207
X = BF_4, ClO_4, PF_6	X = ClO_4 $T\downarrow = 339$ K, $T\uparrow = 360$ K	208
	X = PF_6 $T\downarrow = 242$-269 K, $T\uparrow = 249–287$ K, various samples	207
${}^{1}_{\infty}\{[\mathrm{Fe(L^{62})_3](3\text{-}O_2NC_6H_4SO_3)_2{\cdot}3H_2O}\}^{d}$	Irreversible LS ⟶ HS transition with loss of H_2O at $T \approx 350$ K (magnetic data) or $T \approx 370$ K (optical detection)	209
${}^{1}_{\infty}\{[\mathrm{Fe(L^{62})_3](3\text{-}O_2NC_6H_4SO_3)_2}\}^{d}$	$T\downarrow = 100$ K, $T\uparrow = 110$ K, incomplete transition, 15% HS < 50 K, T is shifted with pressure from 100 K at 1 bar to 270 K at 8.9 kbar	209
${}^{1}_{\infty}\{[\mathrm{Fe(L^{63})_3](4\text{-}Cl\text{-}3\text{-}O_2NC_6H_4SO_3)_2{\cdot}2H_2O}\}^{d}$	$T\downarrow = 120$ K, $T\uparrow = 168$ K, very wide hysteresis loop, incomplete transition, 16% HS < 50 K, pressure dependence $T\downarrow = 250$ K, $T\uparrow = 290$ K at 1.24 kbar	210
${}^{1}_{\infty}\{[\mathrm{Fe(L^{63})_3](4\text{-}Cl\text{-}3\text{-}O_2NC_6H_4SO_3)_2}\}^{d}$	Gradual spin transition between 293 and 50 K	210
${}^{1}_{\infty}\{[\mathrm{Fe(L^{64})_3]X_2{\cdot}\mathit{x}H_2O}\}^{d}$ X = BF_4, ClO_4, CF_3SO_3, p-$MeC_6H_4SO_3$, $x = 0.5–3$	Effect of anion and alkyl chain length on T (range, between 160 to 340 K) hysteresis (0 to 20 K) and steepness (few K to 120 K)	199
${}^{2}_{\infty}\{[\mathrm{Fe(NCS)_2(L^{65})_2]{\cdot}MeOH}\}$	2 Perpendicular networks interpenetrate, $100 < T < 250$ K, incomplete transition, 13% HS at 5 K, 66% HS at 293 K	211
${}^{2}_{\infty}\{[\mathrm{Fe(NCS)_2(L^{66})_2]{\cdot}0.5MeOH}\}$	3 Mutually perpendicular nets interpenetrate, $60 < T < 200$ K, incomplete transition, 50% HS at 60 K, 85% HS at 293 K	212
${}^{3}_{\infty}\{[\mathrm{Fe(L^{67})_3](ClO_4)_2}\}$	Two step conversion corresponding to 50% of Fe each, 2 Fe sites in lattice, $T_1\downarrow = 182$ K, $T_1\uparrow = 185$ K, $210 < T_2 < 240$ K	213
${}^{2}_{\infty}\{[\mathrm{Fe(NCS/Se)_2(L^{67})_2]{\cdot}H_2O}\}$	NCS: $T\downarrow = 123.5$ K, $T\uparrow = 144.5$ K (very abrupt) no spin transition for dehydrated compound	214
	NCS: $T\downarrow = 125$ K, $T\uparrow = 140$ K	215
	NCSe: $T\downarrow = 211$ K, $T\uparrow = 217$ K, from temp. var. ^{1}H NMR	

[a] Arbitrarily ordered with increasing dimensionality. [b] From temperature variable magnetic and/or Mössbauer measurements unless noted otherwise. [c] Temperature value given in parentheses for $T\downarrow$ and $T\uparrow$ defines the abruptness of the transition as the temperature range in which 80% of the iron(II) undergo the transition ($\Delta T_{80}\downarrow$ and $\Delta T_{80}\uparrow$). [d] Structure not fully known, see **15** and text.

to low-spin conversion are usually temperature-variable magnetic and/or Mössbauer measurements. Table 2 lists examples of polymeric networks with spin-crossover behavior and the relevant parameters. It is noteworthy that the spin-transition phenomena and temperature can depend highly on the presence or absence of solvent of crystallization.



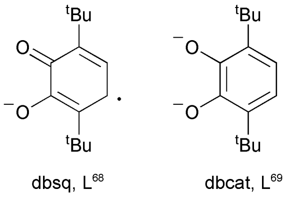
The 1D structures of triazole bridged Fe-polymers are typically not supported by a single-crystal X-ray study but deduced from EXAFS (extended X-ray absorption fine structure),[200] WAXS (wide angle X-ray scattering)[201] or the related (same ligand) 1D crystal structures with other metals.[209,210] The structure of the $[Fe(1,2,4\text{-triazole})_3]^{2/3+}$ cations most probably consists of linear chains in which the neighboring iron atoms are triply bridged by the triazole ligands through the 1,2-nitrogen positions, as depicted in **15**.



15

Related to spin-crossover is the case of compound ${}^{1}_{\infty}\{[Co^{III}(dbsq)(dbcat)(pyz)]\cdot{}^{n}C_6H_{14}\}$ (dbsq = 3,6-$^{t}Bu_2$-1,2-benzosemiquinonate, L[68]) which presents a chain formed through the bridging action of pyrazine and undergoes a reversible temperature- or light-induced shift in the charge distribution from Co(III) and dbcat (~catecholate, L[69]) to Co(II) and dbsq (eqn. (7)). This shift is accompanied by a spin transition from low-spin Co(III) to high-spin Co(II) and a concomitant increase in metal-ligand bond lengths by about 0.2 Å. The light-induced transition [at −35(5) °C] propagates the bond length change, as a photomechanical effect, also along the Co-pyrazine polymer chain to give a change of 0.06 mm per millimeter of polymer length.[216]

In the mixed-valence polymer ${}^{2}_{\infty}\{[N^{n}Pr_4][Fe^{II}Fe^{III}(C_2O_2S_2)]\}$ a phase transition occurs at 110 K on cooling and 120 K on heating (magnetic susceptibility and heat capacity measurements) due to an electron transfer between t_{2g}^{5}-$Fe^{III}S_6$–$Fe^{II}O_6$-$t_{2g}^{4}\,e_g^{2}$ (>120 K) and t_{2g}^{6}-$Fe^{II}S_6$–$Fe^{III}O_6$-$t_{2g}^{3}\,e_g^{2}$ (< 110 K) and a subsequent change in spin-state of the whole system.[217]



$$\underset{t_{2g}^{6}e_g^{0}}{Co^{III}(dbsq)(dbcat)(pyr)} \xrightleftharpoons{\Delta,\ h\nu} \underset{t_{2g}^{5}e_g^{2}}{Co^{II}(dbsq)_2(pyr)} \qquad (7)$$

Non-linear optics (NLO)

Non-linear optical (NLO) materials are used in frequency conversion and intensity modulation of light. Inorganic metal oxides, *e.g.* $LiNbO_3$, or phosphates, *e.g.* KH_2PO_4 (KDP), $KTiOPO_4$ (KTP), are current workhorses for second harmonic generation (SHG, frequency doubling).[45]

NLO materials can be based on coordination polymers that fulfil both requirements of containing organic ligands with large molecular first hyperpolarizabilities, β, and having ordered, non-centrosymmetric structures.[45,226] Ideal NLO chromophores typically contain a good electron donor and acceptor connected through a conjugated bridge. In practice, combining such unsymmetrical bridging ligands with metal centers has led to a somewhat rational synthesis of non-centrosymmetric 3D diamondoid and 2D grid structures.[227] The second harmonic generation is usually studied by using the 1064 nm fundamental wavelength of a Nd:YAG laser using the Kurtz–Perry powder method. Examples are collected in Table 3.

A general problem of NLO materials with organic components, however, may be their long-term stability in the laser light. Occasionally, NLO properties of coordination polymers are reported for "their solutions".[18,228] Yet, because of the degradation of a coordination polymer upon dissolution, these solution properties are not characteristic of the solid-state material.

Porous coordination polymers, porosity, zeolitic behavior

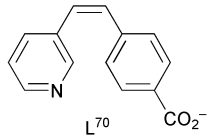
Of special interest in the design of coordination polymers is the search for stable nano- or microporous networks.[24] Porous materials are crystalline or amorphous solids which allow for the reversible passage of molecules through their structures *via* holes in their surface. Considerable efforts are being undertaken to generate three-dimensional metal-organic porous structures. Porosity is the basis for zeolitic behavior, such as functional group or size selective sorption, molecular recognition, gas storage or catalysis (see above). Porous coordination polymers would be functional organic zeolite-analogues,[57,229–231] of the important zeolite materials which find wide-spread application in absorption (molecular sieves), shape- and size-selective heterogeneous catalysis[232] and ion exchange.[46,233]

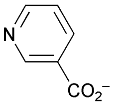
No coordination polymer is directly obtained as a material with *empty* pores large enough for guest incorporation since nature tends to avoid empty space. Stable crystal structures should have a packing coefficient above 0.6 with the majority of crystals having packing coefficients between 0.65–0.77 (*cf.* 0.74 for the cubic and hexagonal closest packed structures of spheres).[234] The description of a coordination polymer as *porous* usually means that cavities exist within the metal-ligand framework. Initially, however, these pores are filled with solvent or other molecules (*e.g.* free ligand) or the counterions. These guest molecules can be seen as templates which in turn may also determine to some extent the size and shape of the cavities.[197c,235] These guest species are not covalently bound to the framework and could, in principle, be removed if they are neutral. Counterions can be exchanged with other charged species or thermally removed with changes in the charge or

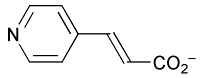
Table 3 Coordination polymers with non-linear optical effects

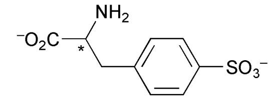
Coordination polymer[a]	Second harmonic generation (SHG) efficiency, $I^{2\omega}$; comment[b]	Ref.
$^2_\infty$\{[4-\{(4-Me$_2$N or 4-MeO)-α-styryl\}-*N*-alkylpyridinium][M^{II}Cr^{III}(ox)$_3$]\}(M = Mn, Fe, Co, Ni, Cu; alkyl = Me, Et, ^{i}Pr, Et$_2$C, C$_7$H$_{15}$)	Up to 100 *vs.* urea; measured at λ = 1900 nm; the stilbazolium-shaped NLO chromophores are however not part of the 2D [M^{II}Cr^{III}(ox)$_3$] network	146
$^3_\infty$\{[Zn(L^{70})$_2$]·0.5H$_2$O\}	6 *vs.* α-quartz	79
$^2_\infty$[Zn(L^{71})$_2$]	2 *vs.* α-quartz	218
$^3_\infty$[Zn(ino)$_2$]	d_{eff} = (1.2 ± 0.6) 10^{-12} m V^{-1}, 3 *vs.* KDP	219
$^3_\infty$[Zn(L^{72})$_2$]	126 *vs.* α-quartz	220
$^1_\infty$[Zn(L^{73})(H$_2$O)$_2$]	Similar to urea and 8–10 *vs.* H$_2$L^{73}; the sulfonate group on L-phenylalanine enhances the SHG intensity about 4–6 *vs.* the zinc complex with L-phenylalaninato (without the sulfonate group)	221
Zr-based surface multilayers with organophosphonate-terminated polar azo dyes L^{74} and L^{75}	β = 150 × 10^{-30} esu and 1060 × 10^{-30} esu; the phosphonate groups are assumed to bridge the zirconium atoms to a 2D layer, the exact structure being unknown[223]	222
$^2_\infty$[Ag(L^{76})]	d_{33} = $^1/_2\chi_{\text{ccc}}$ = (6 ± 3) × 10^{-15} m V^{-1}; same order of magnitude *vs.* α-quartz; determined on oriented single crystals, abolute SHG signal intensity 2 W cm^{-2} ± 20%	77
$^3_\infty$\{[Cd$_2$(SO$_4$)$_2$(4,4′-bipy)$_2$(H$_2$O)$_3$]·3H$_2$O\}	¼ *vs.* KH$_2$PO$_4$	224
$^2_\infty$[Cd(L^{77})$_2$]	1000 *vs.* α-quartz, larger than that of LiNbO$_3$ (600 *vs.* α-quartz)	218
$^3_\infty$\{[Cd(L^{72})$_2$]·H$_2$O\}	18 *vs.* α-quartz; about KDP	220, 219
$^3_\infty$\{[Cd(L^{78})$_2$]·H$_2$O\}	310 *vs.* α-quartz	220
$^2_\infty$\{[Cd$_3$(μ$_3$-OH)(L^{79})$_3$(py)$_6$](ClO$_4$)$_2$\}	10 *vs.* KDP; chiral 2D network, octupolar NLO chromophor (3-fold rotational symmetry)	78
$^2_\infty$\{[Eu(L^{34})$_3$(H$_2$O)$_3$]·H$_2$O\}	17 *vs.* urea	103

[a] Arbitrarily ordered by mass of metal atom. For ox, ino, 4,4′-bipy see Fig. 3; py = pyridine. [b] Determined by Kurtz–Perry powder method with Nd:YAG laser (λ = 1064 nm) unless noted otherwise. $I^{2\omega}$[urea] ≈ $I^{2\omega}$[KDP, KH(D)$_2$PO$_4$] ≈ 10$I^{2\omega}$[α-quartz].[227,225]

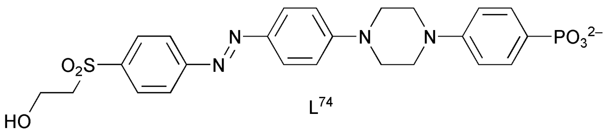

L^{70}

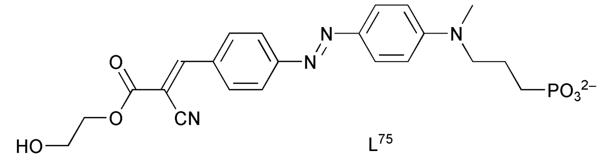

L^{71}

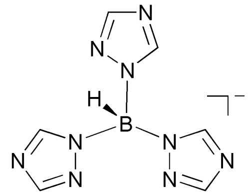

L^{72}


4-sulfonato-L-phenylalaninato

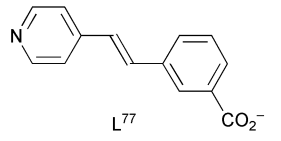
L^{73}

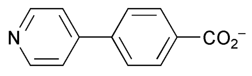

L^{74}

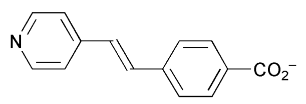

L^{75}


hydro-tris(1,2,4-triazolyl)borate

L^{76}


L^{77}


L^{78}


L^{79}

oxidation state of the host lattice, for example through (de)protonation.[236] Possible applications for such microporous structures include separation, adsorption or heterogeneous catalysis. Catalytic uses of porous networks are described in the section *catalysis*. Yet, compared to zeolites coordination polymers are built with weaker metal-ligand bonds and are inherently less stable. Therefore, functions have to be sought with coordination polymers that are not possible with inorganic oxide materials. Thus, organic zeolites are also hoped for to exhibit novel chemical or physical properties, such as chiral recognition, redox activity or spontaneous polarity formation, which are different from the conventional inorganic zeolites.[57,237,238] The construction of inner cavities and channels that are mainly surrounded by organic components is attractive, since the shape, size, and function of the cavity become designable. Organic ligands allow for a wide variability in architecture. The geometry and the hydrophobic and –philic character of the pores can be tailored.[57,229–231,233] Coordination polymers are just one approach or strategy towards the construction of porous organic solids.[238–241] The covalent coordinative bonds between metal ions and organic ligands offer greater mechanical strength over purely organic lattices with hydrogen bonding. One of the drawbacks in the design of extended porous organic frameworks is the collapse of the host structure upon guest removal (1st generation compounds).

An important criteria for a coordination polymer to be termed porous is that the framework structure is retained intact (2nd generation compounds) or changes dynamically in a well-defined way (3rd generation compounds) in the guest-free state and when exposed to a new guest species as usually proven by X-ray powder diffraction (XRPD).[229] Further control experiments are the monitoring of the crystal morphology or shape to exclude the possibility of recrystallization when the guest exchange is carried out in solution. Also, there is a necessity to distinguish between guests absorbed into the host and those adsorbed onto the host's surface. This may be done by washing procedures and/or by comparing host materials of widely different outer surface areas such as microcrystalline powder *versus* macrocrystalline crystals. The relative molar guest : host ratio should be found in reasonable agreement for both morphologies if there is guest *ab*sorption. In addition, a nonporous structure of similar building blocks, hence similar surface structure could be compared for its sorption properties and should, of course, show no *ab*sorption.[242]

While many coordination polymers are now termed 'porous' on the basis of guest filled cavities or a *static* host–guest structure, the investigation of the guest exchange is somewhat rarer. We will restrict the examples given here to such investigations with a well-proven guest *exchange*. Studies where the guest species were only shown to be removable and the host framework to remain intact but with no proven guest re-uptake will not be mentioned due to space limitations. Studies involving porous systems towards catalytic properties are gathered separately under the heading *Catalysis*.

With respect to the pore dimensions and volume it should always be stated how these values were derived, whether or not the van der Waals radii of the atoms were taken into account. A possible way is to compute the volume as the potential solvent/guest accessible area in the solvent/guest depleted structures,[243] *e.g.* with the program PLATON.[244] Guest removal is usually followed by thermogravimetric analysis/differential thermoanalysis (TGA/DTA). Guest (competition) binding studies in solution are typically monitored by gas chromatography (GC) or NMR of the guest solutions (quantification through internal standards). NMR studies can also be carried out on the host–guest complex, for example, by dissolution (and determination of the ligand : guest ratio) or by ^{13}C solid-state MAS NMR (diamagnetic network). For anion exchange studies, infrared spectroscopy features prominently.

Work on porous coordination polymers towards the aspects of selective sorption is clearly dominated by multitopic (benzene) carboxylate ligands, *e.g.* btc or 1,4-bdc, which have led to the formation of relatively robust "zeolitic" frameworks.[24,230] The ligand 4,4′-bipy is used to some extent. The approach to use longer bridging ligands, which in principle should result in spacious voids, is not necessarily successful because a dense *interpenetrating* structure often forms which contains only small or no channels.[33] *Interpenetration* is the phenomenon of periodic entanglement of two or more independent albeit symmetry-related, identical frameworks with no covalent bonds between the individual frameworks.[25] The entanglement serves to fill the empty space and is guided by weak non-covalent interactions. Disentanglement is only possible by breaking intra-framework connections.[25,245] Mostly, the result of interpenetration is a dense structure. Cases are, however, known where interpenetrating networks create cavities still large enough for guest inclusion (see also entries in Table 4),[85,242,246–251] albeit possibly also sealed-off.[252] Porosity combined with interpenetration is attractive as it provides for a rather robust host framework. Examples of guest-exchanges or guest-removal/absorption studies are listed in Table 4.

A variety of metal(II) dicarboxylate compounds with metal = Cu, Mo, Ru was found to absorb N_2, O_2, Ar or CH_4 besides the zinc(II) 1,4-benzene-dicarboxylate (1,4-bdc) frameworks given in Table 4.[253] A trend towards the investigation of coordination polymers as light-weight methane gas storage devices can be noted. A further trend is the increased utilization of flexible porous frameworks (3rd generation) which can adapt—within certain limits—their structure to the needs of the guest molecules.[260,254]

From metal-containing tetra(4-pyridyl)porphyrin or tetra(4-carboxylphenyl)porphyrin and possibly other building blocks metalloporphyrin-zeolite analogues, *i.e.* network structures with large (solvent filled) channels could be constructed, albeit with varying lattice stabilities.[282]

The reaction of desolvated networks with substrate molecules was used as a basis for shape-selective sensors. Particles of $_{\infty}\{[Zn(O_3PR)]\cdot H_2O\}$ are anchored on a quartz crystal microbalance and thermally dehydrated at 100 °C. These derivatized sensors react rapidly with gaseous ammonia or primary amines.[223]

From 3-pyridine-azocalix[4]arene and $[Pd(en)(H_2O)_2]^{2+}$ a coordination polymeric metallogel (of unknown extended structure) formed which uptakes neutral organic solvent molecules from the aqueous phase in a molar ratio of gel to solvent of ~1 : 10^3. The metallogel was stable in a variety of hydrophilic (*e.g.* thf, dmf, $PhCH_2OH$, CH_3COOH and dmso) and hydrophobic solvents (*e.g.* $CHCl_3$, CH_2Cl_2 and toluene) and insoluble in water over a wide pH range (1 < pH < 13).[300]

Miscellaneous and future prospects

From the viewpoint of constructing functional coordination polymers it will also become important to incorporate functional groups in and on the spacer ligand instead of only using CH-containing moieties. A step in this direction can be seen with the use of the multitopic (multimodal) ligands L^{103}–L^{104} which can be viewed as bridging modifications of 2,2′-bipyridine.[22,27,28,33]

One-dimensional coordination polymers constructed from stacked metal-porphyrin complexes with non-symmetrical bridging ligands, $^{1}_{\infty}[Fe(tpp)(\mu\text{-}L^{106})]$ (*cf.* **3**, tpp = tetraphenylporphyrinate) have been suggested as possible ferroelectric materials. The necessary permanent dipole moment originates from the metal atom being displaced from the porphyrin plane by the action of axial ligands. An aligned orientation of the bridging ligand L^{106} gave the necessary crystallization in a polar, non-centrosymmetric space group.[45]

Redox-active coordination polymers were obtained by incorporating redox-active ferrocene groups into the spacer ligand, such as in L^{107}.[301] Combination of L^{107} with $AgPF_6$ or $M(hfac)_2$ (M = Mn, Cu, Zn; hfac = hexafluoroacetylacetonate) gave the 1D chain compounds $^{1}_{\infty}\{[Ag(L^{107})](PF_6)\cdot 2MeCN\}$ or $^{1}_{\infty}[M(hfac)_2(L^{107})]$, respectively, whose solid-state redox properties were investigated by using a carbon-paste working electrode in cyclic voltammetry.[302]

Lamellar metal phosphonate compounds of formula $^{3}_{\infty}\{[Zr(L^{108})]X_2\}$ (X = Cl, Br, I) (bulk material or thin film) have been used to study photoinduced electron transfer. Photolysis of the white crystalline solids results in the formation of a blue bipyridinium radical cation, followed by oxidation of a halide anion to the radical. The phosphonate groups are assumed to bridge the zirconium atoms to a 2D lamellae, the biphosphonate then bridges between lamellae, the exact structure being unknown.[92,303]

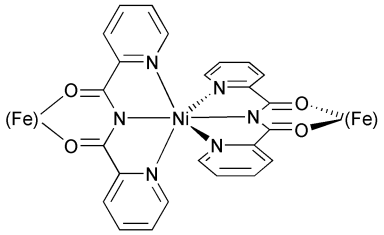
From a water or dmf solution of $^{1}_{\infty}\{[Zn(H_2O)_2(4,4'\text{-bipy})(L^{65})_2](NO_3)_2\cdot 1.75(L^{65})\cdot 0.25(4,4'\text{-bipy})\cdot 4.45H_2O\}$ nanofibers were obtained in an electrospinning process.[304]

Summary

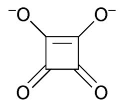
If one would have to single out classes of coordination polymers which have been investigated most with respect to their properties and, thus, appear most promising in view of applications these would be the metal-oxalate nets, $^{2}_{\infty}\{[M^{II}M^{III}(ox)_3]^{-}\}$ as magnetic materials, the Fe-triazole chains, $^{1}_{\infty}\{[Fe(L^{60-64})_3]^{2+}\}$ as spin-crossover materials, the multitopic benzene-carboxylate (bdc, btc) or 4,4′-bipyridine frameworks as zeolitic materials. It is evident that these compounds are based on the rather simple, commercially available ligands oxalate, 1,2,4-triazole, benzene-1,3- or -1,4-dicarboxylate (isophthalate, 1,3-bdc or terephthalate, 1,4-bdc), benzene-1,3,5-tricarboxylate (btc) or 4,4′-bipyridine (4,4′-bipy). This dwarfs the

Table 4 Examples of guest-exchanges or guest-removal/absorption studies

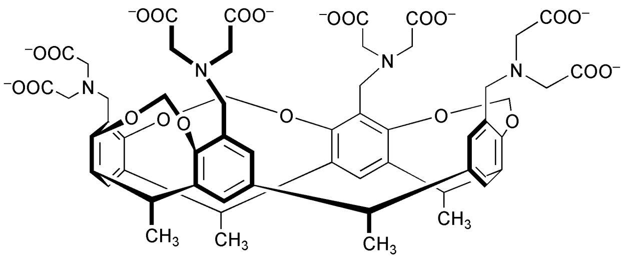
Coordination polymer^{a,b}	Guest-exchange; comments^{c,d}	Ref.
$^{2}_{\infty}\{[Fe^{II}\{Ni^{II}(L^{80})_2\}_{1.5}](ClO_4)_2\cdot 4.5CHCl_3\cdot 3MeOH\cdot 10H_2O\}$	$ClO_4^- \longrightarrow PF_6^-$, $CHCl_3 \longrightarrow CHBr_3$; channel dim. 12 × 13 Å^2	255
$^{3}_{\infty}\{[Co_5(imidazolate)_{10}]\cdot 2{}^{i}PrCH_2OH\}$	$\square \rightleftarrows 2{}^{i}PrCH_2OH \longrightarrow EtOH$, toluene, xylene; channel dim. 9.4 × 3.9 Å^2, therm. stab. < 430 °C	256
$^{3}_{\infty}\{[Co_3(\mu_3\text{-}OH)_2(L^{81})_2]\cdot 3H_2O\}$	$H_2O \rightleftarrows \square$; channel dim. 7.5 × 7.5 Å^2, therm. stab. < 405 °C	257
$^{2}_{\infty}\{[M_4Co_4(L^{82})_2]\cdot xH_2O\}$ ($x \sim 40$) (M = Ca, Sr, Ba)	$H_2O \rightleftarrows \square$; channel diameter × length; pore diam. × length, Å^2: for Ca: 10 × 5.4; 10 × 21, for Sr: 13 × 11; 10 × 27.5, for Ba: 11 × 11; 9 × 27	258
$^{2}_{\infty}\{[Co(Hbtc)(py)_2]\cdot 2/3py\}$	py $\rightleftarrows \square \longrightarrow C_6H_6$, $PhNO_2$, PhCN, PhCl, not MeCN, $MeNO_2$, $C_2H_4Cl_2$; channel dim. 7 × 10 Å^2, therm. stab. < 350 °C	259
$^{2}_{\infty}\{[Co(NCS)_2(L^{83})_2]\cdot 4solv\}$ solv = Me_2CO, thf	solv $\rightleftarrows \square \longrightarrow$ tetrahydropyran, 1,4-dioxane, not linear ethers (Et_2O, $^{n}Pr_2O$, $^{i}Pr_2O$, $^{t}BuOMe$), not ring hydrocarbons (cyclopentane, cyclohexane, C_6H_6), not linear alkanes (pentane, hexane, heptane); channel dim. 3.5 × 10.5 Å^2, 3rd gen. compd.	260
$^{3}_{\infty}[M_3(btc)_2(H_2O)_{12}]$ M = Co, Ni, Zn	$H_2O \rightleftarrows \square \longrightarrow NH_3$, aqua ligands removed, not CO, CO_2CS_2, H_2S, MeCN, pyridine; channel dim. 4 × 5 Å^2, therm. stab. < 500 Å^2	261
$^{2}_{\infty}\{[M_2(NO_3)_4(4,4'\text{-bipy})_3]\cdot xH_2O\}$ M = Co, Ni, $x = 4$; Zn, $x = 2$	(M = Co) $H_2O \longrightarrow \square \longrightarrow CH_4 > N_2 \approx O_2$; channel dim. 3 × 6 and 3 × 3 Å^2	262
$^{2}_{\infty}\{[Ni_2(NO_3)_4(4,4'\text{-bipy})_3]\cdot EtOH\}$ (3D through H-bonding)	EtOH $\rightleftarrows \square$; therm. stab. < 230 °C	263
$^{2}_{\infty}\{[\{Ni(L^{84a})\}_3(L^{45})_2]\cdot 16H_2O\}$	$H_2O \longrightarrow [Cu(NH_3)_4](ClO_4)_2$, not $[Cu(en)_2](ClO_4)_2$, $H_2O \longrightarrow \square \longrightarrow MeOH > EtOH >$ PhOH, not C_6H_6, toluene; 3rd gen. compd.; binding constants determined	264
$^{2}_{\infty}\{[\{Ni(L^{84b})\}_3(L^{45})_2]\cdot 14H_2O\}$	$H_2O \longrightarrow \square \longrightarrow$ EtOH selectivity, not acetone, MeCN, MeOH, thf, C_6H_6, toluene; channel dim. 8.3 × 7.6 Å^2, 24% porosity, therm. stab. < 200 °C	265
$^{1}_{\infty}\{[Ni(4,4'\text{-bipy})_{2.5}(H_2O)_2](ClO_4)_2\cdot 1.5(4,4'\text{-bipy})\cdot 2H_2O\}$	$ClO_4^- \longrightarrow PF_6^-$; channel dim. 11 × 11 Å^2	266
$^{3}_{\infty}\{[Ni(L^{85})(OH)_2(H_2O)_2]\cdot 2H_2O\}$	$H_2O \rightleftarrows \square$; also aqua ligands removed; channel diameter 4–8 Å, therm. stab. < 380 °C	267
$^{2}_{\infty}\{[\{Cu(cyclam)\}_3(btc)_2]\cdot 18H_2O$	$H_2O \longrightarrow EtOH > MeOH > PhOH$, not, toluene; binding constants determined, channel diameter 8 Å, therm. stab. < 195 °C	268
$^{2}_{\infty}[Cu(1,4\text{-bdc})]$	$\square \longrightarrow Ar$, CH_4; channel dim. 6 × 6 Å^2, BET surface area 545 m^2 g^{-1}	269
$^{2}_{\infty}[Cu(L^{47})]$	$\square \longrightarrow Ar$, CH_4; channel dim. 5.4 × 5.4 Å^2, BET surface area 416 m^2 g^{-1}	269
$^{2}_{\infty}[Cu(L^{86})]$	$\square \longrightarrow Ar$, CH_4; channel dim. 5 × 5 Å^2, BET surface area 347 m^2 g^{-1}	269
$^{3}_{\infty}[Cu(1,4\text{-bdc})(dabco)]$	$\square \longrightarrow Ar$, CH_4; channel dim. 7.4 × 7.4 Å^2, BET surface area 1548 m^2 g^{-1}, therm. stab. < 343 K	270
$^{2}_{\infty}\{[Cu(4,4'\text{-bipy})_2(H_2O)_2]SiF_6\}$ (2-fold interpenetration)	In part $SiF_6^{2-} \longrightarrow GeF_6^{2-}$; channel dim. 2 × 2 Å^2	271
$^{3}_{\infty}\{[Cu(EF_6)(4,4'\text{-bipy})_2]\cdot 8H_2O\}$ (E = Si, Ge)	$H_2O \longrightarrow \square \longrightarrow Ar$ (E = Si); $H_2O \longrightarrow \square \longrightarrow CH_4$; channel dim. 8 × 8 and 6 × 2 Å^2, BET surface area 1337 m^2 g^{-1} (E = Si), therm. stab. < 150 °C,	272
	Higher CH_4 abs. capacity than in zeolites	271
$^{3}_{\infty}\{[Cu_2(PF_6)(NO_3)(4,4'\text{-bipy})_4](PF_6)_{1.4}(NO_3)_{0.6}\cdot 2H_2O\cdot 1.2EtOH\}$	H_2O, EtOH $\longrightarrow \square \longrightarrow N_2$; channel dim. 4 × 3 and 3 × 3 Å^2, BET surface area 559 m^2 g^{-1}	271
$^{2}_{\infty}\{[Cu_2(O_2CCH_3)_4(L^{87})]\cdot 3C_6H_6\}$	$C_6H_6 \rightleftarrows \square$; channel dim. 20 × 9.5 Å^2, pore vol. 40%, therm. stab. < 180 °C	273
$^{2}_{\infty}\{[Cu_2(L^{88})_2(L^{89})]\cdot 8H_2O\}$	$H_2O \rightleftarrows \square \longrightarrow MeOH$, not CH_4; channel dim. 4 × 6 Å^2, pore vol. 33 %, BET surface area 37 m^2 g^{-1}, therm. stab. < 220 °C	274
$^{3}_{\infty}\{[Cu_2(L^{88})_2(L)]\cdot xH_2O\}$ L = pyz, $x = 2$; 4,4′-bipy, $x = 5$; or L^{83}, $x = 5$	$H_2O \longrightarrow \square \longrightarrow CH_4$; channel dim. 4 × 6 Å^2 (pyz), 9 × 6 Å^2 (4,4′-bipy), 10 × 6 Å^2 (L^{83}), therm. stab. < 260 °C	275
$^{3}_{\infty}\{[Cu_3(btc)_2(H_2O)_3]\cdot H_2O\}$ (x~10)	$H_2O \longrightarrow \square \longrightarrow H_2O$, pyridine, also aqua ligands removed; channel dim. 9 × 9 Å^2, 40% accessible porosity, BET surface area 692 m^2 g^{-1}, therm. stab < 240 °C	276
$^{3}_{\infty}\{[Cu_3(L^{90})_2(H_2O)_3]\cdot 9dmf\cdot 2H_2O\}$ (2-fold interpenetration)	dmf,$H_2O \longrightarrow \square \rightleftarrows N_2$, Ar, CO, CH_4, CH_2Cl_2, CCl_4, C_6H_6 or C_6H_{12}; pore diameter 16.4 Å, aperture joining pores 7.7 × 14 Å, 67% accessible porosity, Langmuir surface area 1502 m^2 g^{-1}, therm. stab < 250 °C	277
$^{3}_{\infty}\{[Cu(ino)_2]\cdot 2H_2O\}$	$H_2O \longrightarrow \square \longrightarrow$ MeOH, EtOH > ^{n}PrOH, not alkanes, aromatics; 3rd gen. expandable structure, therm. stab. < 300 °C	278
$^{3}_{\infty}\{[Cu_2(L^{91})(H_2O)_2]\cdot 4H_2O\}$	$H_2O \longrightarrow \square \rightleftarrows N_2$, Ar, $\square \longrightarrow CH_2Cl_2 \gg C_6H_6 > CCl_4 > C_6H_{12}$ (rate constants determined), also aqua ligands removed; channel diameter 6–6.5 Å, Langmuir surface area 560 m^2 g^{-1}, therm. stab. < 260 °C	279
$^{3}_{\infty}\{[Cu(4,4'\text{-bipy})_{1.5}]NO_3\cdot 1.25H_2O\}$ (2-fold interpenetration)	$NO_3^- \longrightarrow SO_4^{2-}$, BF_4^- (by IR, elemental analysis); channel dim. 8 × 6 and 4 × 5 Å^2, therm. stab < 180 °C	249
$^{3}_{\infty}\{[Cu(CF_3SO_3)_2(4,4'\text{-bipy})_2]\cdot H_2O\cdot 2CH_2Cl_2\}$ (2-fold interpenetration)	$\square \longleftarrow H_2O,CH_2Cl_2 \longrightarrow CCl_4$, amyl acetate, 4-Me-2-pentanone, *n*-decane, $MeNO_2 \longrightarrow \square$; 3rd gen. expandable struct., pore vol. 23%, therm. stab. < 270 °C	251
$^{3}_{\infty}\{[Cu_2(L^{92a})_2(H_2O_2)]\cdot 8dmf\cdot 2H_2O\}$	dmf,$H_2O \longrightarrow CHCl_3$, C_6H_6, MeCN, MeOH, EtOH, THF, DMSO, pore vol. 79%	280
$^{2}_{\infty}\{[ZnCu(1,3\text{-bdc})_2(H_2O)_3(dmf)]\cdot dmf\}$	dmf $\longrightarrow H_2O$, also dmf ligands replaced; guest coordination sites at channel walls	281
$^{2}_{\infty}\{[Zn(1,4\text{-bdc})(H_2O)]\cdot dmf\}$	H_2O,dmf $\longrightarrow \square$ (3D framework?) $\rightleftarrows N_2$, CO_2, CH_2Cl_2, CH_3Cl, C_6H_6, C_6H_{12}; pore diameter 5–7 Å, Langmuir surface area 270–310 m^2 g^{-1}, therm. stab < 315 °C	237, 283
$^{3}_{\infty}\{[Zn_3(1,4\text{-bdc})_3(MeOH)_4]\cdot 2MeOH\}$	MeOH $\rightleftarrows \square \longrightarrow N_2$, Ar, CO_2, CH_2Cl_2, CH_3Cl, CCl_4, C_6H_6, C_6H_{12}, MeOH > EtOH > ^{n}PrOH, NH_3, $MeNH_2$, Me_2NH, not MeCN, Me_3N, pore diameter 8 Å, surface area 140 m^2 g^{-1}	237, 284
$^{3}_{\infty}\{[Zn_4O(1,4\text{-bdc})_3]\cdot 8dmf\cdot PhCl\}$	dmf,PhCl $\longrightarrow CH_3Cl \longrightarrow \square \longrightarrow N_2$, Ar, CH_2Cl_2, CH_3Cl, CCl_4, C_6H_6, C_6H_{12}; pore diameter 8–12 Å, pore vol. 55–60%, surface area 2900 m^2 g^{-1}, therm. stab < 300 °C	237, 285
$^{3}_{\infty}\{[Zn_4O$(1,4-bdc derivatives and analogues, see L^{92}-series)$_3]\cdot x$dmf$\cdot xCHCl_3\}$	variation of pore size with L^{92} ligands, solvent $\longrightarrow \square \rightleftarrows N_2$, $\square \longrightarrow CH_4$, CH_2Cl_2, CCl_4, C_6H_6, C_6H_{12}; pore diameter 3.8 to 28.8 Å, pore vol. 56 to 91%, therm. stab. < 400 °C, (isoreticular metal-organic frameworks, IRMOF's)	286
$^{2}_{\infty}\{[2H_3O][Zn_3(\mu_3\text{-}O)(L^{1D})_6]\cdot 12H_2O\}$ (**1**, and L^4 see catalysis) (homochiral framework)	$H_3O^+ \longrightarrow Na^+$, K^+, Rb^+, (from L-isomer) H_3O^+, $H_2O \longrightarrow \Delta/\Lambda\text{-}[Ru(2,2'\text{-bipy})_3]^{2+}$ with preferential incorporation of the Δ-form (66% ee); triangular channels with ~13 Å side length, pore volume ~47%	54
$^{3}_{\infty}\{[Zn_3(OH)_2(L^{92b}$ or $L^{92c})_2]\cdot 4def\cdot 2H_2O\}$ (def = diethylformamide)	def,$H_2O \longrightarrow \square \longrightarrow$ def, C_6H_6, not N_2, Ar, def,$H_2O \rightleftarrows C_6H_6$, $CHCl_3$, ^{i}PrOH, THF, toluene; pore vol. 66%, therm. stab. < 150 °C (L^{92c}), < 250 °C (L^{92b})	287



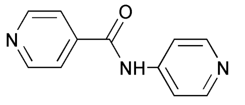
Ni(L^{80})$_2$



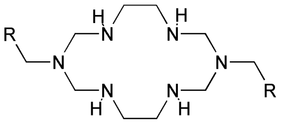
dianion of
squaric acid
L^{81}

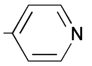


L^{82}

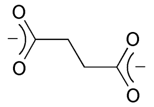


N-pyridin-4-yl-isonicotinamide
L^{83}

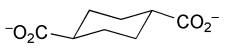


R =  L^{84a}

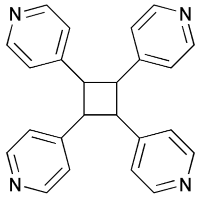
R = CH_3 L^{84b}



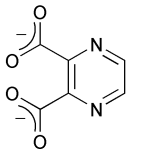
dianion of succinic acid
L^{85}



L^{86}

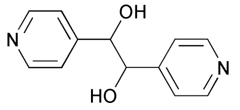


L^{87}

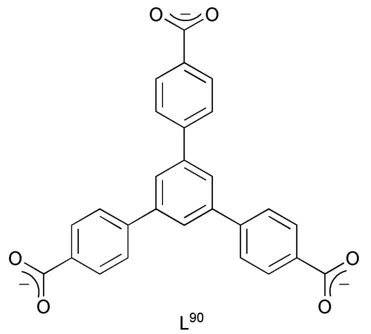


pyrazine-2,3-dicarboxylate

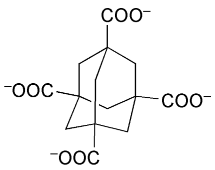
L^{88}



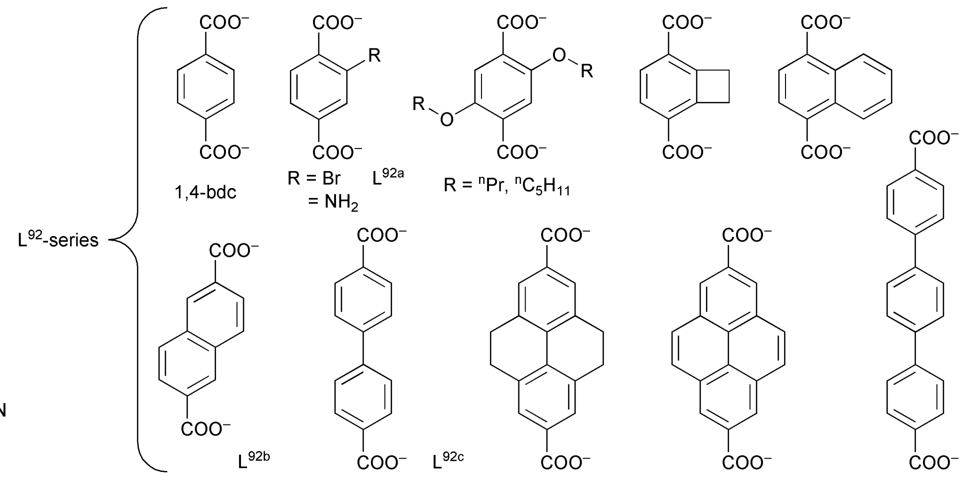
L^{89}

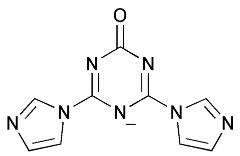


L^{90}

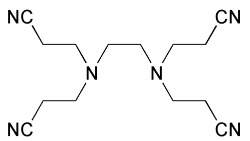


1,3,5,6-adamantane-
tetracarboxylate
L^{91}

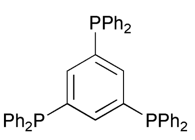




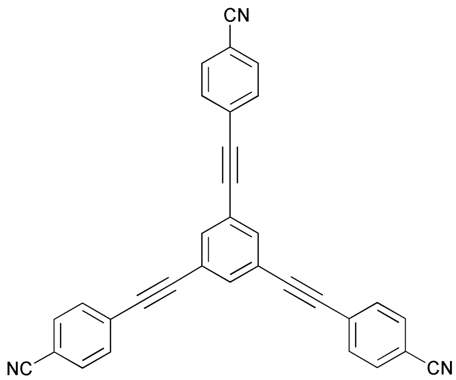
L^{93}



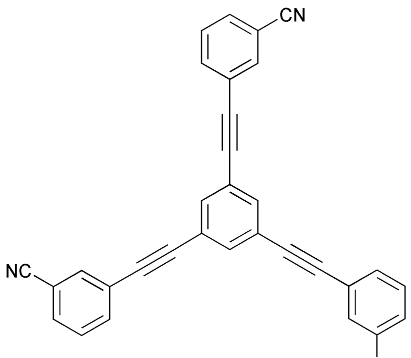
L^{94}



L^{95}



1,3,5-tris(4-ethynyl)benzonitrile
L^{96}

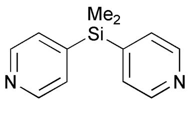


1,3,5-tris(3-ethynyl)benzonitrile
L^{97}

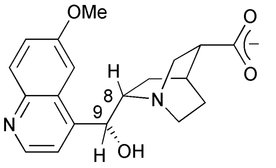
Table 4 *Contd.*

Coordination polymer[a,b]	Guest-exchange; comments[c,d]	Ref.
${}^{3}_{\infty}\{[Zn_2(btc)NO_3]\cdot H_2O\cdot 5EtOH\}$	H_2O,EtOH ($\longrightarrow\square$) $\longrightarrow$ MeOH, EtOH, ^{i}PrOH, ^{n}BuOH, ^{t}BuOH, dmf, not ${}^{t}BuC_6H_4OH$, $CHCl_3$, 1,2-$C_2H_4Cl_2$, MeCN, $PhNO_2$, PhCN, $PhCH_3$, acetone, MeC(O)Et; pore vol. 44%, cross sect. 14 Å, therm. stab < 460 °C	288
${}^{3}_{\infty}\{[Zn(L^{93})_2]\cdot x\mathrm{dmf}\}$ ($x \sim 6$)	dmf $\longrightarrow$ MeCN $\longrightarrow \square$; channel dim. 9.6 × 5.5 Å^2, therm. stab. < 300 °C	289
${}_{\infty}\{[Zr_2(L^3)(O^tBu)_2]\cdot x\mathrm{thf}\}$	thf $\longrightarrow \square \longrightarrow N_2$, AcOEt > C_6H_6 > hexane, methyl vinyl ketone, acrolein, 1,3 cyclohexadiene, alkyl acrylate (alkyl = Me, Et, ${}^{n}C_6H_{13}$, ^{t}Bu); pore diameter 7 Å, surf. area 200 m^2 g^{-1}	52
${}^{2}_{\infty}\{[Ag(L^{94})]CF_3SO_3\}$	$CF_3SO_3^- \rightleftarrows NO_3^-$ with phase change to ${}^{1}_{\infty}\{[Ag(L^{94})]NO_3\}$, $CF_3SO_3^-$, $NO_3^- \longrightarrow ClO_4^-$ with phase change to ${}^{3}_{\infty}\{[Ag(L^{94})]ClO_4\}$(3rd gen. structure)	290
${}^{3}_{\infty}\{[Ag(4,4'\text{-bipy})]NO_3\}$ (3-fold interpenetration)	$NO_3^- \rightleftarrows PF_6^-$, MoO_4^{2-}, BF_4^-, SO_4^{2-}; channel dim. 23 × 6 Å^2, therm. stab < 238 °C	291
${}^{2}_{\infty}\{[Ag_4(L^{95})_3](CF_3SO_3)_4\cdot xMeNO_2\cdot xEtOH\}$	$MeNO_2$,EtOH $\longrightarrow \square \longrightarrow Et_2O$, H_2O; channel diameter 16 Å, 36% access porosity, accessible surface area 1032 m^2 g^{-1},therm. stab. < 400 °C	292
${}^{3}_{\infty}\{[Ag(CF_3SO_3)(L^{96})]\cdot 2C_6H_6\}$ (6-fold interpenetration)	$C_6H_6 \longrightarrow C_6D_6$, $C_6H_6 \rightleftarrows$ toluene, undecane, $PhCH_2OH$; channel dim. 15 × 22 Å^2 $C_6H_6 \rightleftarrows \square \longrightarrow$ vapor of $PhCH_2OH$, $PhCH(OH)CH_3 > C_6H_6$, *m*-xylene ⩾ undecane,	293, 242
${}^{2}_{\infty}\{[Ag(CF_3SO_3)(L^{97})]\cdot 2C_6H_6\}$	$C_6H_6 \rightleftarrows \square$; pore vol. 57%, therm. stab. < 200 °C	294
${}^{2}_{\infty}\{[Ag(L^{15})]ClO_4\cdot 2MeNO_2\}$ (homochiral network)	$MeNO_2 \rightleftarrows H_2O$; pore vol. 52%	81
${}^{2}_{\infty}\{[Ag_3(L^{98})_4](NO_3)_3\cdot H_2O\}$ (2-fold interpenetration)	$NO_3^- \rightleftarrows NO_2^-$; channel dim. 7 × 8 Å^2, therm. stab. < 200 °C	295
${}^{3}_{\infty}\{[Cd(ino)_2(EtOH)]\cdot EtOH\}$ (2-fold interpenetration)	EtOH $\rightleftarrows \square$	247
${}^{3}_{\infty}[Cd(8S,9R\text{-}L^{99})_2]$ (homochiral framework)	$\square \rightleftarrows$ (*S*)-2-butanol, enantiomer sep. from *rac*-2-butanol with 98.2% ee, therm. stab. < 265 °C; $\square \rightleftarrows$ (*S*)-2-methyl-1-butanol, enantiomer separation from *rac*-mixture with (9?)8.4% ee	58
${}^{3}_{\infty}\{[La_2(L^{100})_3(H_2O)_4]\cdot 6H_2O\}$	$H_2O \rightleftarrows \square$, also aqua ligands are partially removed, therm. stab. < 160 °C	296
${}^{3}_{\infty}\{[Tb_2(1,4\text{-bdc})_3(H_2O)_2]\cdot 2H_2O\}$	$H_2O \rightleftarrows \square \longrightarrow NH_3$, also aqua ligands are removed; not CO, N_2, therm. stab < 450 °C	106
${}^{3}_{\infty}\{[Tb_2(1,4\text{-bdc})_2(NO_3)_2(dmf)_2]\cdot 2dmf\}$	dmf $\longrightarrow \square \rightleftarrows CO_2$, $\square \longrightarrow$ MeOH > EtOH > ^{i}PrOH, also dmf ligands are removed; therm. stab. < 320 °C	297
${}^{3}_{\infty}\{[Tb_2(L^{101})_3(dmso)_4]\cdot 16dmso\}$ (2-fold interpenetration)	dmso $\longrightarrow \square \longrightarrow CHCl_3 \longrightarrow \square \longrightarrow$ dmf $\longrightarrow \square \longrightarrow$ dmso, also dmso ligands are removed; channel dim.'s 7.5 × 6.7 Å^2 and 7.1 × 5.7 Å^2, free vol. 71%	246
${}^{3}_{\infty}\{[Tb(H_2L^{44})_{0.5}(L^{44})_{0.5}(H_2O)]\cdot 2H_2O\}$	Channel dim. 12 × 11.2 Å^2	298
${}^{3}_{\infty}\{[Er_2(L^{44})_{1.5}(H_2O)_4]\cdot 4H_2O\}$	Channel dim. 9.1 × 7.1 Å^2	298
${}^{3}_{\infty}\{[Yb_4(L^{44})_3(H_2O)_8]\cdot 6H_2O\}$	Channel dim.'s 15.2 × 5.6 Å^2 and 8.5 × 3.4 Å^2, $H_2O \rightleftarrows \square$; therm. stab. < 430 °C	298
${}^{2}_{\infty}\{[Pb(L^{102})]NO_3\cdot 1.35H_2O\}$	$NO_3^- \longrightarrow {}^{15}NO_3^- \longrightarrow I^-$	299

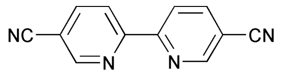
[a] Arbitrarily ordered by mass of metal atom. For 4,4′-bipy, 1,3-bdc, 1,4-bdc, btc, dabco, ino, pyz see Fig. 3; dmf = dimethylformamide, en = ethylenediamine, py = pyridine. [b] Native state including guest molecules from synthesis. [c] Host framework identity checked by X-ray powder diffraction (XRPD) and stable framework (2nd generation compound)[229] unless noted otherwise; □ indicates guest exchange proceeds *via* the guest-free or partially guest-depleted host framework as intermediate. Channel dimensions are given as approximate values. [d] The thermal stability if given refers to the guest-free host framework as usually determined by thermogravimetric analysis/differential thermoanalysis (TGA/DTA).



L^{98}

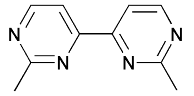


8*S*,9*R*-L^{99}



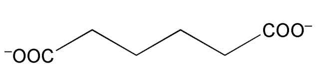
5,5′-dicyano-2,2′-bipyridine

L^{103}



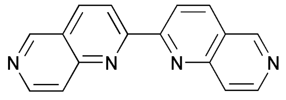
2,2′-dimethyl-4,4′-bipyrimidine

L^{104}



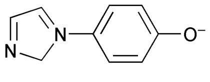
adipato

L^{100}

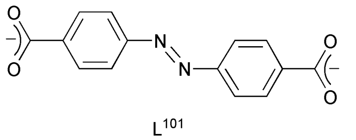


2,2′-bi-1,6-naphthyridine

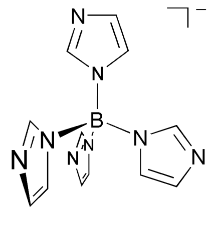
L^{105}



L^{106}

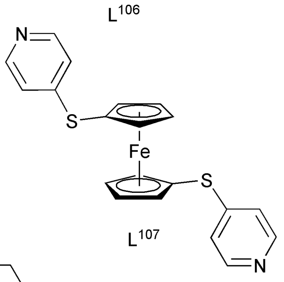


L^{101}

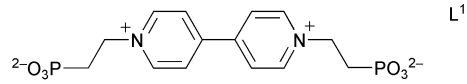


tetrakis(imidazolyl)borate

L^{102}



L^{107}



L^{108}

many attempts to design ever new and special organic ligand systems. Obviously, a fine-tuning of the properties will not so much involve new ligands but crystal engineering of the above parent systems in terms of counter ions, guest templates, crystallization conditions (solvent, time, temperature) *etc.*

Along these lines it may be predicted that applications of coordination polymers will not necessarily include stucturally well-defined compounds but metal-ligand combinations that "work", irrespective of a known three-dimensional structure. Catalytic studies seen with coordination polymers, *e.g.* employing a Ru(II)/1,4-diisocyanobenzene system[50] or the structurally ill-defined metallogels[56] (see under *Catalysis*), or the spin-transition work on the Fe-triazolato compounds are just the more prominent examples.

The future will show which of the above or maybe even other, not yet recognized, applications are in there for metal-organic coordination networks. And I am very confident that there will be applications for an even brighter future of coordination polymeric materials.

Acknowledgements

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