Coordination polymers using (2-pyridyl)alkylamine-appended carboxylates: magnetic properties†‡

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It is the intention of this *Perspective* to review the literature involving the synthesis of coordination polymers of varying dimensionality utilizing a class of chelating ligands comprising of (2-pyridyl)alkylamine-appended carboxylates performed in our group and by others. From the standpoint of functional aspects, we will focus on the magnetic properties of the chosen systems. In essence, we will provide a snapshot of this research field.

Introduction

The field of coordination polymers has advanced extensively.[1–14] Coordination polymers are constructed from metal ions (connectors) and tailor-made organic ligands (linkers). As transition metal ions display a range of coordination geometries, they act as versatile connectors[1–3,12,13] and impart, among other things, magnetic and catalytic properties to coordination polymers. Consequently, they can be used as functional materials.[1–3,12,13]

In the majority of coordination polymers, either the O-atoms of anions (carboxylates, nitrates, sulfates, phosphates, phenolates) and/or the N-atoms of cyanates, cyanides, amines or pyridines engage in coordination with transition metal ions.[9] These statistics indicate the importance of pyridine and carboxylate moieties in constructing coordination polymers.[14] Notably, carboxylate groups can assume many types of bridging conformation, the most important being triatomic *syn–syn*, *syn–anti*, *anti–anti* and monoatomic.[15,16] The *syn–syn* conformation favors the generation of binuclear systems whereas *syn–anti* favors the formation of extended structures with varying nuclearity. Thus, carboxylates act as ideal linkers between metal ions for the propagation of metal–ligand coordination units due to their divergent bridging capabilities (Scheme 1).

The importance of the (2-pyridyl)alkylamine moiety as a ligand in coordination chemistry in general and in bioinorganic chemistry in particular is well recognized.[17–32] We present in this article coordination polymers synthesized from a systematically varied class of (2-pyridyl)alkylamine-appended carboxylate functionalities (Fig. 1). A given bridging coordination mode of the carboxylate, constrained by coordination of the (2-pyridyl)alkylamine unit to a metal ion, helps predict the direction of propagation. It should be appreciated that

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† Dedicated to Professor R. L. Dutta.

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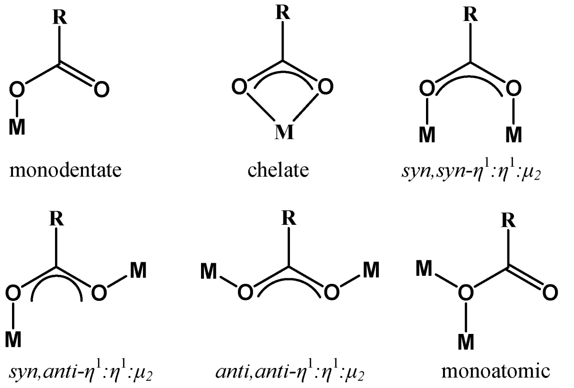


Scheme 1 The monodentate and bidentate chelating mode and bridging conformations for carboxylate groups.

(2-pyridyl)alkylamine-appended carboxylate ligands (Fig. 1) provide 'rigid' (albeit flexible, due to the variable methylene spacer within N2/N3 chelating donor sites, and between the chelating donor sites and the carboxylate functionality) metal–ligand coordination units. Utilizing the chosen ligands (Fig. 1), which combine the two functional groups, has proven to be very useful in the synthesis of not only new coordination polymers but also tetra- and multi-metallic cores (see below). The coordination polymers of (2-pyridyl)alkylamine-appended carboxylate ligands are well populated with metal ions such as Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Ln(III), and have yielded interesting magnetic properties.

The systems and their magneto-structural properties

The polymer topology generated from the self-assembly[9] of inorganic metal ions and organic chelating ligands is controlled by a combination of the structure and conformation of the chosen ligands, the coordination geometry preferred by the

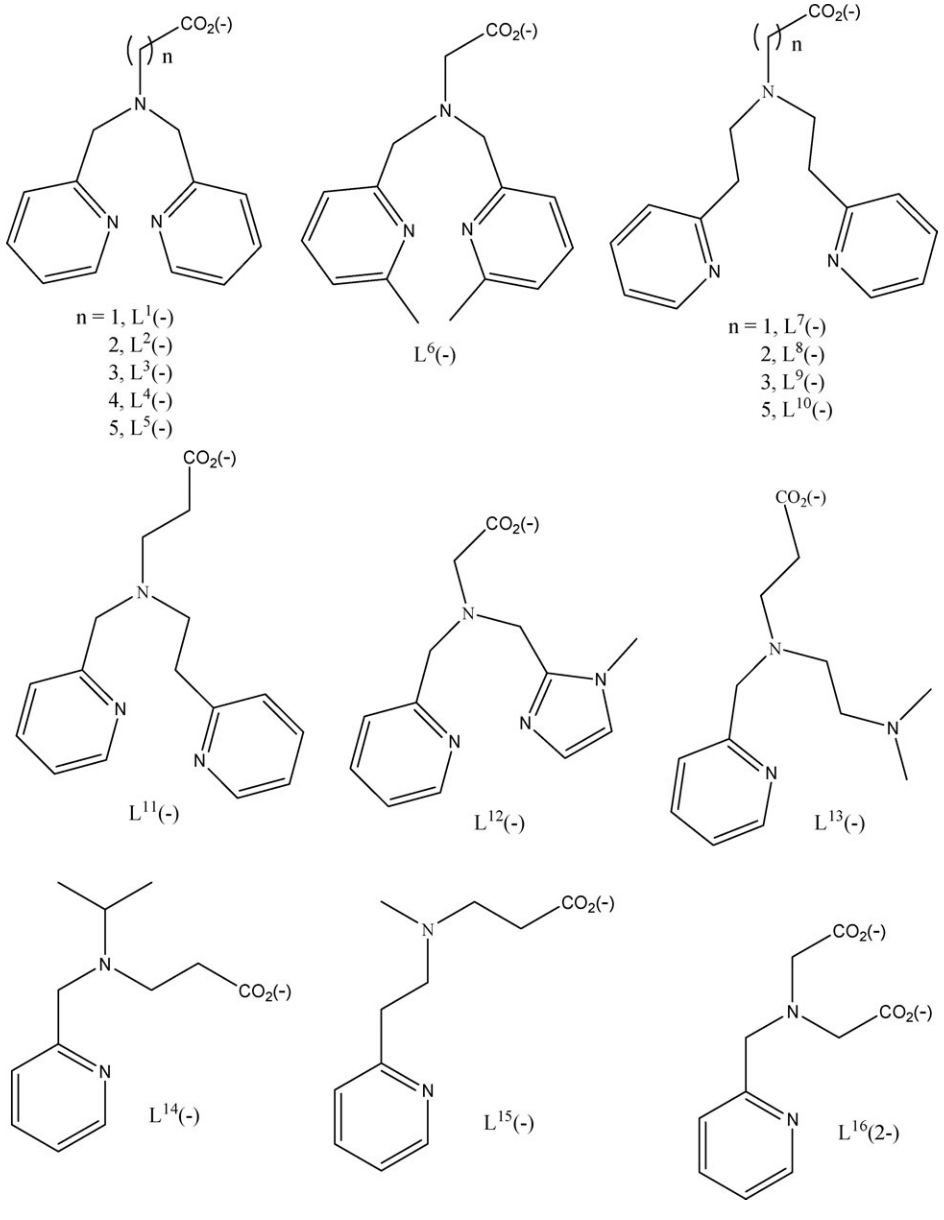


Fig. 1 The ligands pertinent to this article.

metal ion, the influence of the counterions, the solvent system, the reaction temperature, and sometimes the metal-to-ligand ratio.[14] The important characteristics of connectors and linkers are the number and orientation of their binding sites, which decide coordination numbers and coordination geometries, respectively. The chemical attributes of organic ligands play a very important role in dictating polymer framework topology,[14] as it serves to tether the metal centers and to propagate the structural information expressed in metal coordination preferences throughout the extended structure. It should be mentioned here that although several coordination polymers have been designed to date and several useful functional properties have been discovered, the predictability of the network geometry of coordination polymers is still a challenging problem.[9]

We now present an overview of the structure–property relationships (magneto-structural trends) of coordination polymers synthesized using the ligands $L^1(-)$ to $L^{16}(2-)$, in sequence. We briefly present a structural description of the specific compounds, followed by a discussion of their magnetic properties.[1–3,13] We think it is best to discuss the over-arching structural trends.

The majority of coordination polymers utilizing (2-pyridyl)-alkylamine-appended carboxylate ligands belong to the one-dimensional (1D) topology (see below). The primary reason could be the mode of coordination of the chosen ligands (tridentate: two pyridyl N and a carboxylate O; tetradentate: three pyridyl N and a carboxylate O) to a given metal ion and an additional bridging carboxylate O to link to the nearest neighbour. Thus, the disposition of the ligand donor atoms predetermines the formation of 1D coordination polymers. Triggered by the coordination demand of a given metal ion, one or more solvent molecule(s) can complete the coordination sphere.

It is appropriate to mention here that the ligands $L^7(-)$, $L^{14}(-)$ and $L^{15}(-)$ have so far not afforded any coordination polymers; however, the formation of discrete tetrameric carboxylate-bridged Cu^{II}_4 complexes has been accomplished.[33–35] Notably, $L^{11}(-)$ provides both a 1D coordination polymer (see below)[34] as well as a discrete tetramer.[35] It should be mentioned here that in generating figures to highlight the metal coordination environment and coordination polymeric backbone, we have consistently followed the color code: C, grey; N, blue; O, red; M^{n+}, grey green/turquoise. Amongst the reported systems, to reveal the nature and extent of magnetic-exchange interactions, temperature-dependent magnetic susceptibility measurements were performed on only a few of them. Notably, the existence of both antiferromagnetic and ferromagnetic [the energy gap between the singlet and the triplet state is expressed in terms of J in cm^{-1}; the magnetic exchange coupling constant (J) is positive for ferromagnetic and negative for antiferromagnetic interactions between two adjacent metal centers], and also spin-canting, behavior has been observed for the chosen systems (see below).

The five-membered chelate ring forming potentially tetradentate ligands $L^1(-)$ to $L^5(-)$ afforded the carboxylate-bridged 1D polymeric chain complexes $[Cu^{II}(L^1)][ClO_4]\cdot H_2O$ (**1**),[36] $[Cu^{II}(L^2)][ClO_4]\cdot 2H_2O$ (**2**),[36] $[Cu^{II}(L^3)(H_2O)][ClO_4]\cdot 3H_2O$ (**3**),[36] $[Cu^{II}(L^4)(H_2O)][ClO_4]$ (**4**)[37] and $[Cu^{II}(L^5)(H_2O)][ClO_4]$ (**5**).[37] The copper(II) ions are sequentially bridged by *syn–anti* carboxylate groups. In **1** and **2**, the three nitrogen donor atoms and an oxygen atom belonging to the carboxylate group of an adjacent molecule form the basal plane. An oxygen atom of the appended carboxylate group of the ligand provides an axial coordination, and hence completes five-coordination around the copper. The bridging carboxylate is in the basal–axial (or equatorial–axial) mode. In **3–5**, the three nitrogen atoms of the ligands and an oxygen atom belonging to the carboxylate group of an adjacent molecule form the basal plane. A water molecule as an axial ligand completes the five-coordination around the copper. Two neighbouring carboxylate groups coordinate to two Cu^{II} centers in the basal–basal (or equatorial–equatorial) mode. The longer alkyl tether between the carboxylate group and the bis(2-pyridylmethyl)amine unit most likely makes it entropically unfavorable to form an intramolecular chelate with the carboxylate moiety. Perspective views of **1**, **3**, and **5** are shown in Fig. 2. From Fig. 2, it appears that only **1** has a *syn–anti* carboxylate O–C–O bridge. However, this may not be the case in examples **2–5**. This apparent disparity is due to the differential coordination of the carboxylate-appended ligands L^1–L^5. While in **1** and **2** a carboxylate oxygen of the ligand coordinates at the axial position, in **3–5** a water molecule is coordinated at the axial positions. In essence, for ligands L^3–L^5, only one of the two carboxylate oxygens participates in coordination. In each case, the copper(II) center is of a distorted [τ = 0.25 (**1**), 0.19 (**2**), 0.15 (**3**), 0.09 (**4**) and 0.06 (**5**); values of 0 and 1 are indicative of

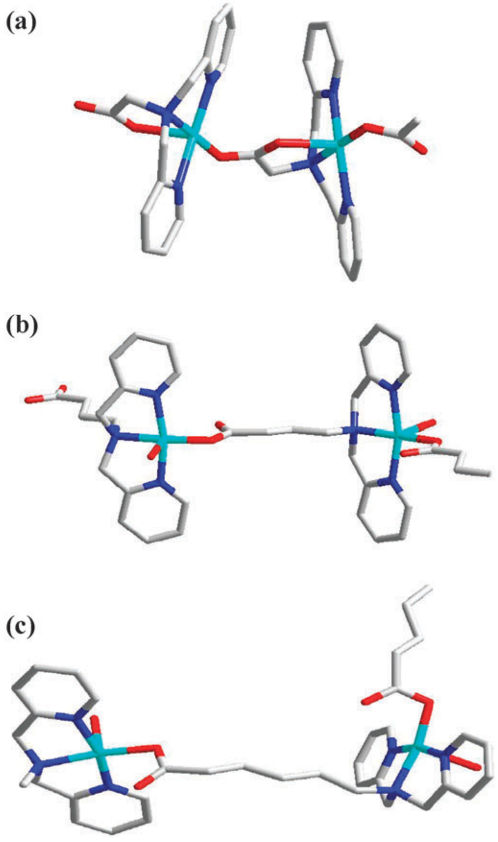


Fig. 2 Representation of the 1D coordination polymer of (a) $[Cu^{II}(L^1)][ClO_4]\cdot H_2O$ (**1**), (b) $[Cu^{II}(L^3)(H_2O)][ClO_4]\cdot 3H_2O$ (**3**) and (c) $[Cu^{II}(L^5)(H_2O)][ClO_4]$ (**5**).

idealized square-pyramidal and trigonal-bipyramidal geometries, respectively][38] square-pyramidal CuN_3O_2 coordination geometry. One obvious observation is that the longer the carboxylate-appended chain the less is the distortion from ideal square-pyramidal geometry. The J values of **1–5** are +0.21, +0.14, +0.09, +0.03 and +0.06 cm^{-1}, respectively.[36,37] In the case of the short O–C–O bridge (ligands with a short aliphatic tether), the magnetic interactions between the neighbouring Cu^{II} centers are mediated *via* the carboxylate bridge. For complexes supported by ligands with long aliphatic tethers, the spin communication is operative between chains, transmitted by hydrogen-bonding interactions (see below).

The cationic part of $[Mn^{II}_2(L^2)_2(H_2O)(MeCN)][BPh_4]_2\cdot 2MeCN$ (**6**)[39] consists of 1D chains, in which the Mn^{II} ions are bridged by carboxylates in a bidentate *syn–anti* mode. These chains extend along the *c* axis (Fig. 3). The minimum repetition unit of the cationic chain contains two "$Mn^{II}(L^2)$" units. The high-spin Mn^{II} ions in **6** are weakly antiferromagnetically-coupled [$J = -0.20(1)\ cm^{-1}$].[39]

The five-membered chelate ring forming a potentially tetradentate ligand $L^6(-)$ [closely similar to $L^1(-)$ to $L^5(-)$, but the pyridyl rings are substituted by methyl groups at the 6-position in $L^6(-)$] afforded the *syn–anti* carboxylate-bridged 1D polymeric zigzag chain complex $[Mn^{II}(L^6)(H_2O)][PF_6]$ (**7**).[40] In **7**, the geometry at the Mn^{II} ion is distorted octahedral, surrounded by three nitrogen donor atoms (two pyridyl and a tertiary amine) and a carboxylate oxygen of $L^6(-)$, a water molecule and a carboxylate oxygen of an adjacent molecule (Fig. 4). These chains run parallel to each other, and the pyridine moieties form couples of long π–π interactions (Fig. 4).[41,42] This arrangement shows a pseudo-2D magnetic structure with a major interaction pathway along the chain ($J = -0.12\ cm^{-1}$) and an inter-chain minor one ($zJ' = -0.004\ cm^{-1}$; z is the number of nearest neighbours).[40]

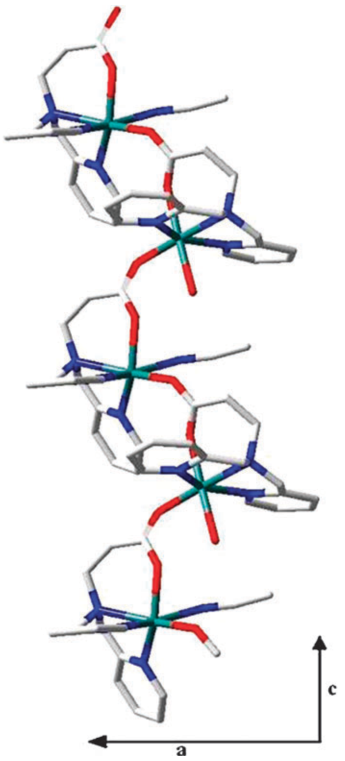


Fig. 3 View of the 1D cationic chain of $[Mn^{II}_2(L^2)_2(H_2O)(MeCN)][BPh_4]_2\cdot 2MeCN$ (**6**). The chain extends along the *c* axis.

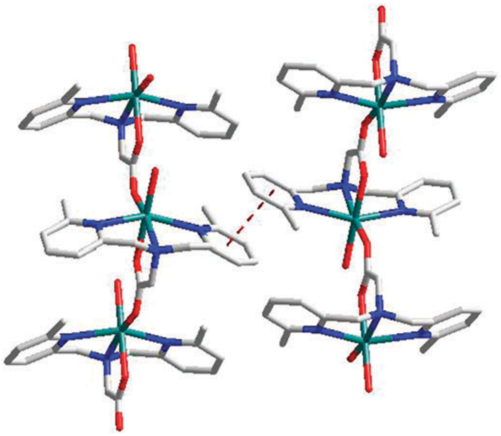


Fig. 4 Two adjacent chains running along the *a* axis with the π–π interaction between the pyridyl rings of $[Mn^{II}(L^6)(H_2O)][PF_6]$ (**7**).

The six-membered chelate ring forming potentially tetradentate ligands $L^8(-)$ to $L^{10}(-)$ gave rise to the carboxylate-bridged 1D polymeric chain complexes $[Cu^{II}(L^8)][ClO_4]\cdot H_2O$ (**8**),[33] $[Cu^{II}(L^9)(H_2O)][ClO_4]$ (**9**)[33] and $[Cu^{II}(L^{10})][ClO_4]\cdot H_2O$ (**10**).[33] As observed for **1** and **2**, for **8**, the three nitrogen donor atoms, an oxygen atom of the appended carboxylate group of the ligand, and an oxygen atom belonging to the carboxylate group of an adjacent molecule provide five-coordination around the copper. As for **3–5**, in both **9** and **10**, the five-coordination is provided by three nitrogen donor atoms of $L^9(-)$ and $L^{10}(-)$, an oxygen atom belonging to the carboxylate group of an adjacent molecule, and either a water molecule (complex **9**) or a perchlorate oxygen atom (complex **10**). A perspective view of **9**, showing H-bonding interactions with (i) coordinated water and a ClO_4^- counterion in the same chain, and (ii) coordinated water in one chain and a carboxylate group in the next, is displayed in Fig. 5. The copper(II) centers assume a slightly distorted square-pyramidal CuN_3O_2 coordination environment.[38] Within the 1D polymeric chain, the Cu···Cu separation increases as the carboxylate-appended chain length increases. In **9**, the apical position is occupied by a water molecule but in **8** and in **10** it is by a carboxylate oxygen atom.

In $[Mn^{II}(L^{11})(H_2O)][ClO_4]\cdot 2H_2O$ (**11**),[43] the ligand acts as a tetradentate ligand towards a Mn^{II} ion and acts as a monodentate bridging ligand towards a neighbouring Mn^{II} center, utilizing the appended carboxylate group. This coordination arrangement forms a 1D polymeric chain. In **11**, extensive π–π stacking[41] involving alternate pyridine rings of adjacent 1D chains exists, which eventually leads to the formation of a 2D network structure. Ligand $L^{11}(-)$ affords 1D coordination polymers $[Co^{II}(L^{11})(H_2O)][ClO_4]\cdot 2H_2O$ (**12**)[34] (six-coordinate Co^{II}) and $[Cu^{II}(L^{11})][ClO_4]\cdot 2H_2O$ (**13**)[34] (almost a perfect ($\tau = 0.01$)[38] square pyramidal $Cu^{II}N_3O_2$ coordination environment) of closely similar structures. The cases of **12** and **13** are displayed in Fig. 6 and Fig. 7, respectively.

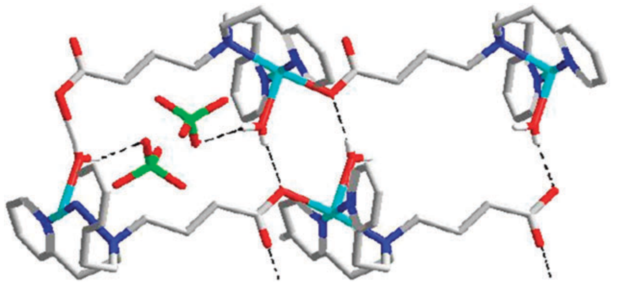


Fig. 5 Perspective view of the 1D polymeric chain of $[Cu^{II}(L^9)][ClO_4]\cdot H_2O$ (**9**), showing H-bonding interactions.

Temperature-dependent magnetic susceptibilities for **11** and **13** revealed antiferromagnetic interactions through *syn–anti* carboxylate bridges between the M^{II} centers [$J = -0.25\ cm^{-1}$ (**11**) and $-0.66(1)$ (**13**)].[34,43] Complex **12** also exhibits an exchange interaction between the M^{II} ions through a *syn–anti* bridging carboxylate pathway.[13,34] Notably, magnetic studies on **12** showed spontaneous magnetization below 5 K (Fig. 8), which corresponds to the presence of spin-canted antiferromagnetism [$J = -2.65(2)\ cm^{-1}$] (Fig. 9).[13,34]

The complex $[Mn^{II}(L^{12})(MeOH)][PF_6]$ (**14**)[44] consists of a polymeric sequence of Mn^{II} ions bridged by *syn–anti* carboxylate groups. A pseudo-octahedral arrangement around the Mn^{II} centers is provided by three nitrogen donor atoms and a carboxylate oxygen atom of $L^{12}(-)$, a methanol molecule and a carboxylate oxygen from an adjacent molecule. Around each Mn^{II} center, two carboxylates bind in a *cis* geometry. This unusual bridging geometry (*syn–anti-cis*) provides a chain running in a zigzag manner along the *b* axis. The structure can be described as a chiral helix-like chain running parallel to the *b* axis (Fig. 10). The crystal packing reveals a layer organization with entangled parallel helices. A pyridine moiety from one helix is parallel to an imidazole from the next, with a small interplanar distance. Like **7**, complex **14** shows a pseudo-2D magnetic structure, with one major pathway along the chain ($J = -0.17\ cm^{-1}$) and an inter-chain minor one ($zJ' = -0.08\ cm^{-1}$).[44]

The structure of $[Cu^{II}(L^{13})][CF_3SO_3]\cdot H_2O$ (**15**)[43] is closely similar to that observed in **13**. The CuN_3O_2 coordination sphere is slightly distorted ($\tau = 0.19$).[38] The copper(II) centers in **15** are weakly antiferromagnetically coupled ($J = -1.88\ cm^{-1}$).[43] In $[Zn^{II}(L^{13})][ClO_4]$ (**16**),[43] each Zn^{II} ion assumes a distorted trigonal-bipyramidal geometry

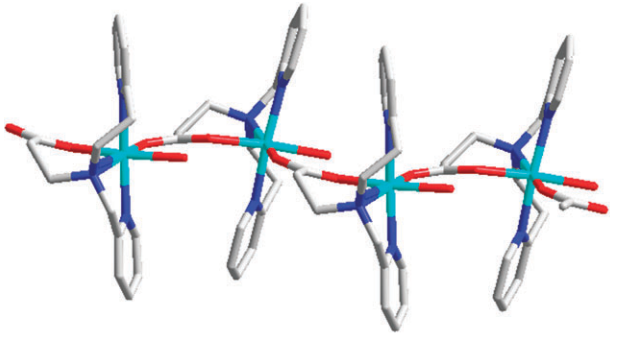


Fig. 6 View of the 1D cationic chain of $[Co^{II}(L^{11})(H_2O)][ClO_4]\cdot 2H_2O$ (**12**).

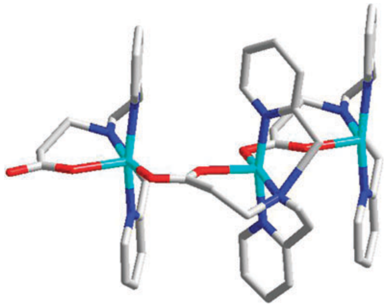


Fig. 7 Representation of the 1D coordination polymer of $[Cu^{II}(L^{11})][ClO_4]\cdot 2H_2O$ (**13**).

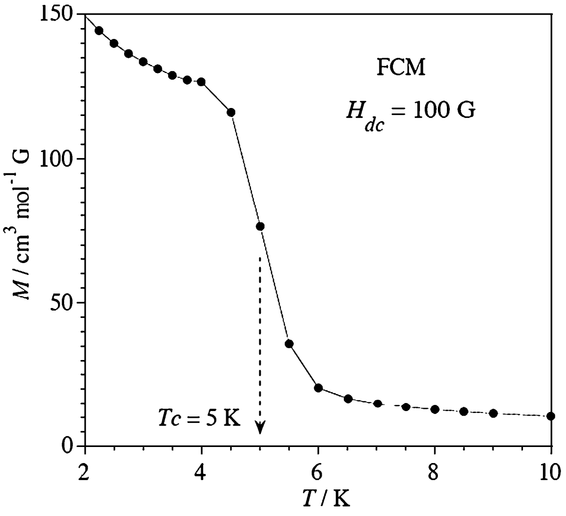


Fig. 8 The field-cooled magnetization of $[Co^{II}(L^{11})(H_2O)][ClO_4]\cdot 2H_2O$ (**12**).

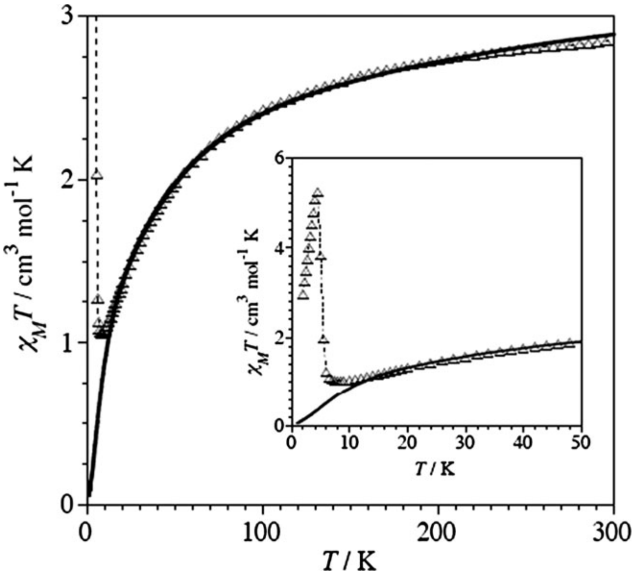


Fig. 9 A plot of $\chi_M T$ *vs.* T for a powdered sample of $[Co^{II}(L^{11})(H_2O)][ClO_4]\cdot 2H_2O$ (**12**). Inset: expanded view of the dependence of the $\chi_M T$ product of **12** in the low temperature (< 10 T) region under 0.01 T.

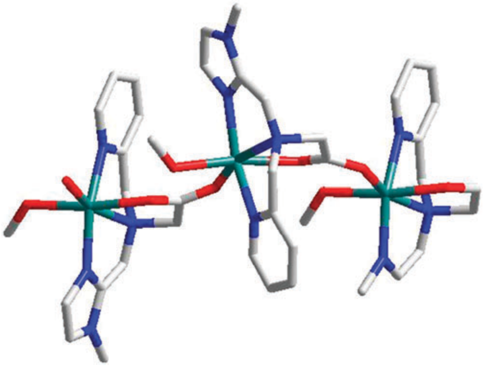


Fig. 10 View of the chiral helix-like chain of $[Mn^{II}(L^{12})(MeOH)][PF_6]$ (**14**) running parallel to the *b* axis.

(τ = 0.60)[38] with two nitrogen atoms and a carboxylate oxygen atom of $L^{13}(-)$ comprising the basal plane, whereas the apical positions are filled by an oxygen atom belonging to the carboxylate group of an adjacent molecule and a tertiary amine nitrogen atom from $L^{13}(-)$. Each zinc(II) ion is coordinated by a *syn–anti* carboxylate bridge to form a 1D polymeric chain.

Complexes $[Co^{II}(L^{16})(H_2O)][ClO_4]\cdot H_2O$ (**17**)[45] and $[Ni^{II}(L^{16})(H_2O)][ClO_4]\cdot H_2O$ (**18**)[45] are isostructural, presenting distorted octahedral geometries around their metal centers. Every two adjacent '$[Co^{II}(L^{16})(H_2O)]$' units are joined by one *anti–anti* bridging carboxylate group to form an infinite 1D chain (Fig. 11). It should be mentioned here that the *anti–anti* bridging mode of carboxylates is relatively uncommon.[16a,45–50] The neighbouring chains of **17** are further connected by O–H···O hydrogen bonds, forming a hydrogen-bonded 2D supramolecular sheet. The adjacent chains also interact with each other by π–π stacking interactions between the adjacent parallel pyridyl rings.[41,42] This leads to the stacking of H-bonded 2D sheets into a 3D supramolecular structure.

The complexes $[Ln^{III}(L^{16})(NO_3)(H_2O)]$ [Ln = La (**19**), Nd (**20**), Sm (**21**), Gd (**22**), Dy (**23**) and Er (**24**)][51] are isostructural coordination polymers of 2D layered networks. The metal center is nine-coordinated (distorted tricapped trigonal prism geometry) by two N atoms and two carboxylate O atoms of an $L^{16}(2-)$ ligand, two bridging carboxylate O atoms of two other $L^{16}(2-)$ ligands from two neighbouring units, two O atoms of one bidentate chelating nitrato ligand, and an O atom of an aqua ligand. Ligand $L^{16}(2-)$ utilizes all its potential donor sites and coordinates to three metal centers as tetradentate and two bridging modes. All the carboxylate groups of $L^{16}(2-)$ take the *syn–anti* bidentate bridging coordination mode. The bridging of two O atoms of one carboxylate group of $L^{16}(2-)$ link two neighbouring lanthanide ions along the *a* axis and the action of the other carboxylate group of $L^{16}(2-)$ links two metal centers along the *b* axis. As a result, a 2D layered network is obtained (Fig. 12), where every adjacent pair of lanthanum ions are linked together by one carboxylate group and each lanthanum ion is connected to four others along the *a* and *b* axes. The 2D network is further assembled into a 3D structure by π–π stacking interactions between pairs of pyridine rings.[41,42]

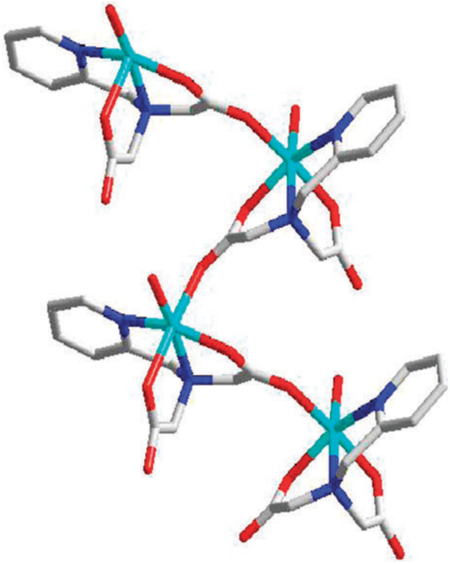


Fig. 11 View of the 1D polymeric chain of $[Co^{II}(L^{16})(H_2O)][ClO_4]\cdot H_2O$ (**17**).

Structure/property trends

Given the structural features presented above, the following statements are in order. (i) Out of the 24 coordination polymers considered here, 10 contain Cu^{II} as the metal ion. (ii) Apart from the case of the Ln(III) systems, which provide a 2D layered network, the majority of systems belong to the 1D coordination polymer category. (iii) Barring only two complexes, all are linked by *syn–anti* carboxylate bridges.

Examination of the magneto-structural data of the carboxylato-bridged coordination polymers[16,34,36,37,43,48,50] reported in the literature have allowed the following generalizations to emerge. The exchange coupling is strongly antiferromagnetic with a *syn–syn* conformation (small metal–metal distance and hence good overlap of magnetic orbitals), very

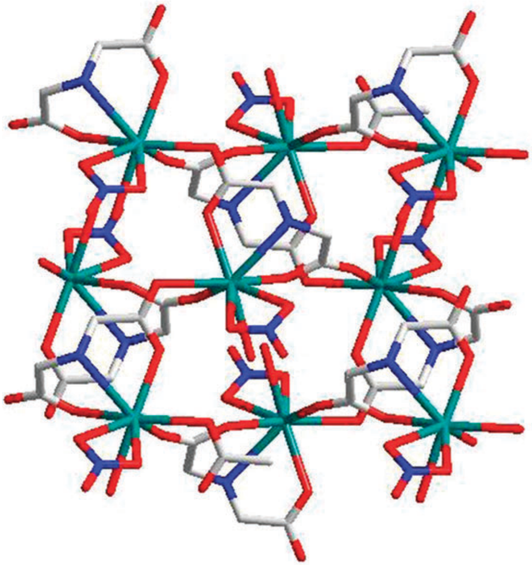
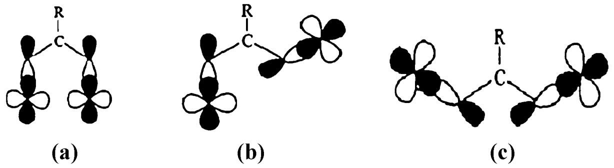


Fig. 12 View of the 2D layered network of $[La^{III}(L^{16})(NO_3)(H_2O)]$ (**19**) along the *c* axis (pyridyl coordination is not shown for clarity).

weakly so (eventually ferromagnetic) with a *syn–anti* conformation and weak to moderately antiferromagnetic with an *anti–anti* conformation. Intuitively, the magnetic coupling constant (J) can be expected to be the sum of both ferromagnetic (J_F) and antiferromagnetic (J_{AF}) contributions.[52]

From the standpoint of magneto-structural trends, we consider first the case of the copper(II) systems. For *syn–anti* conformations, both weak ferromagnetic and antiferromagnetic coupling is observed.[16b,34,36,37,43,50] The observed coupling depends on the structural features of the Cu–O–C–O–Cu′ bridge unit, which controls the overlap of the magnetic orbitals. The non-planarity of this unit is expected to reduce the overlap, which in turn is expected to favor ferromagnetic exchange coupling.[16b,34,36,37,43,50] The nature and extent of coupling also depends on the coordination geometry of the Cu^{II} centers. For a square planar/square pyramidal geometry, the ground state of the Cu^{II} ion is described by the $d_{x^2-y^2}$ orbital and for a trigonal bipyramidal geometry the relevant metal orbital is d_{z^2}. For the basal–basal (or equatorial–equatorial) *syn–anti* conformation, the contributions between the 2p orbitals of the O and O′ atoms belonging to the magnetic orbitals centered on Cu and Cu′ are unfavorably oriented to give a significant overlap (Scheme 2).[16b,34,36,37,43] This would lead to $J_{AF} \approx 0$, so that the weak ferromagnetic interaction becomes predominant. If *syn–anti* carboxylate bridges link an equatorial position of one Cu^{II} ion with an axial position of an adjacent Cu^{II} ion, the magnetic orbital for the Cu^{II} ion in square-pyramidal surroundings (the $d_{x^2-y^2}$ orbital) will have some admixture of the d_{z^2} orbital in a trigonal-bipyramidal geometry. Such a magnetic coupling is expected to be very weak because it is the result of the interaction of a $d_{x^2-y^2}$-type orbital with a d_{z^2}-type orbital, the latter having a very small spin density. This unfavorable orientation of the magnetic orbitals centered on the Cu^{II} ions accounts for the weak ferro-/antiferromagnetic coupling (Scheme 2).[16b,34,36,37,43]

In the light of the structural trends and the orbital interaction considerations discussed above, the nature and extent of magnetic interaction through the *syn–anti* carboxylate bridge observed in Cu^{II} coordination polymers (**1–5**, **13** and **15**) can readily be rationalized. The values of the ferromagnetic coupling constant more or less steadily decrease from **1** to **5**. This fact may be attributed to the increase in the Cu···Cu separation [5.350(1) (**1**), 5.800(2) (**2**), 9.363(2) (**3**), 9.745(3) (**4**) and 10.401(1) (**5**) Å] and the non-planarity of the Cu–O–C–O–Cu′ bridging network. The dihedral angles between the two planes Cu–O–C and Cu′–O–C in **1** and **2** (in both it is an axial–equatorial bridge) are ~9 and ~31°, respectively. Moreover, the dihedral angles of the carboxylate group coordinated to Cu′ and the CuN$_3$O plane are ~66 and ~78° for **1** and **2**, respectively. These structural considerations are expected to increase ferromagnetic coupling in **2** compared to **1**. The reverse result actually observed may be attributed to the decrease in the value of the distortion parameter (τ values: **1**, 0.25; **2**, 0.19). It is to be emphasized here that in the case of the short O–C–O bridge, the magnetic super-exchange is mediated by the carboxylate bridge. However, in many of the other cases (**3–5**), spin communication is operative between chains, transmitted *via* hydrogen-bonding mechanisms involving the bound water in one chain and the carboxylate group in the next (*cf.* Fig. 5). It is worth mentioning here that the packing diagrams of **3** and **4** do not reveal any hydrogen-bonding interactions between the chains. However, in **5**, due to hydrogen-bonding interactions between the chains, the Cu···Cu distance is 5.2356(9) Å [*cf.* within a chain, the Cu···Cu separation is 10.401(1) Å (see above)]. The Cu···Cu distances between chains thus may actually be shorter than through the long aliphatic tethers. Hydrogen bonding-mediated magnetic coupling has been observed in other examples.[53–56] For **13** and **15**, the small overlap between the magnetic orbitals of the Cu^{II} ion through the *syn–anti* carboxylato bridge (in both it is an axial–equatorial bridge) for a Cu–O–C–O–Cu′ skeleton that is not planar [dihedral angle values: **13**, ~3°; **15**, ~22°], the dihedral angles of the carboxylate group coordinated to Cu′ and the CuN$_3$O plane (**13**, ~86°; **15**, ~67°], and the Cu···Cu distance [**13**, 4.579(6) Å; **15**, 5.281(9) Å], account for the weak antiferromagnetic coupling observed.



Scheme 2 The orbital interaction between the metal ion ($d_{x^2-y^2}$-type orbital) and the carboxylate group in (a) *syn–syn*, (b) *syn–anti* and (c) *anti–anti* bridging mode.

We will now consider *syn–anti* carboxylate-bridged coordination polymers containing Mn^{II} ions. The observed weak antiferromagnetism could be explained considering the Mn···Mn distances [**6**: 5.376(4) and 5.282(4) Å; **7**: 5.564(2) Å; **11**: 5.5663(22) Å; **14**: 5.42 Å] and a mismatch in the orientation of the magnetic orbitals.

Complex **12**, the only *syn–anti* carboxylate-bridged coordination polymer containing Co^{II} ions, exhibits spin-canted antiferromagnetism.[13,34] We provide here a rationale for why spin-canting[52,57–59] is present in the case of cobalt. From the viewpoint of magnetic interactions between the nearest neighbours,[52] two possibilities usually arise. If the molecular spins are oriented in a parallel fashion then the interaction is ferromagnetic, and if the spins are oriented in such a way that the two adjacent molecular spins are antiparallel, then the interaction is antiferromagnetic. However, when the symmetry of the crystal structure is low enough, the molecular spins may not be rigorously antiparallel but canted, which gives rise to weak ferromagnetism.[57] The canting observed in **12** is a consequence of distortion of the Co^{II} center from an idealized octahedral geometry and zero-field splitting effects. It is known that zero-field splittings cause single-ion anisotropy and are one of the sources of canting or weak ferromagnetism.[57] We believe that the magnetic behavior observed in **12** is derived predominantly from single-ion anisotropy due to the absence of an inversion centre to relate the Co^{II} ions by symmetry. In fact, the Co–O–C–O–Co′ bridging network appreciably deviates from planarity.[34]

Conclusions and future outlook

We have shown how careful selection of metal–ligand coordination units of varying coordination geometry have allowed us to construct coordination polymers and to study their magnetic properties. In essence, (2-pyridyl)alkylamine-appended carboxylate ligands have proven their great potential in the synthesis of coordination polymers. The successful syntheses of these coordination polymers has primarily enriched *syn–anti* carboxylate-bridged 1D coordination polymers not only structurally, but magnetically as well. In essence, a reasonable understanding of the structures and magnetic properties of a range of coordination polymers has been obtained. They exhibit interesting magnetic properties in the rising area of magnetic materials.[60–62] Future efforts will investigate how the stereochemical demand of this class of ligands can direct the molecular shape and control the magnetic properties of the resulting complexes. Finally, it is worth stating that this work has added strength to the notion that the selection of suitable organic ligands, subject to spatial orientation due to metal–ligand coordination, is a key factor in manipulating the structures of coordination polymers. Opportunities for exciting advances of both intellectual and practical value are still affordable by the great sweep of synthetic chemistry that is at our disposal for creative use in the domain of coordination polymers.

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