Constructing magnetic molecular solids by employing three-atom ligands as bridges

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The combination of some three-atom bridges with paramagnetic 3d transition metal ions results in the systematic isolation of molecular magnetic materials, ranging from single-molecule and single-chain magnets to layered weak ferromagnets and three-dimensional porous magnets. The design strategy and role of secondary components, such as co-ligands, templates and other mixed short ligands are discussed.

1 Introduction

The last decade witnessed the great success in the research of molecule-based magnetic materials.[1] Pure organic magnets,[2] high critical temperatures[3] and bistable spin crossover compounds[4] have been achieved. Furthermore, the discovery and development of single-molecule-magnets (SMM)[5] and single-chain-magnets (SCM)[6] have crossed paramagnetism and long-range ordered magnetism and give a wide range of spin-dynamics. Parallel to these developments and achievements, there is increasing interest in creating materials combining magnetism and other properties such as conductivity, optical properties and most recently, porosity.[7]

The rational design of new molecular magnets requires the consideration of two basic aspects: spin carriers and bridges. For the former, there are not many choices except the pure organic radicals and transition metal ions. We focus our attention on the magnetic 3d transition metal ions such as Mn, Fe, Co, Ni and Cu. These ions, including the isotropic spins (Mn^{2+} and Cu^{2+}), the highly anisotropic ones (Mn^{3+} and Co^{2+}), and one with large residual orbital contribution (Co^{2+}), provide good opportunities for the magnetic investigation, both theoretically and experimentally.

For the bridges on the other hand, the short ligands of one to three atoms, such as O^{2-}, OH^-, CN^-, N_3^-, $HCOO^-$, $C_2O_4^{2-}$, *etc.*, take the key role in magnetic exchange between magnetic centers. Generally, the shorter and the more

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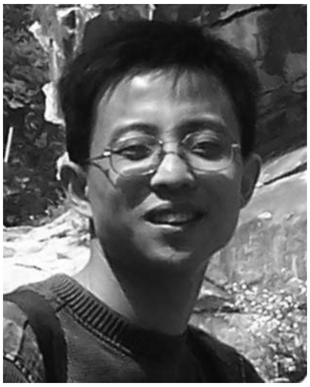
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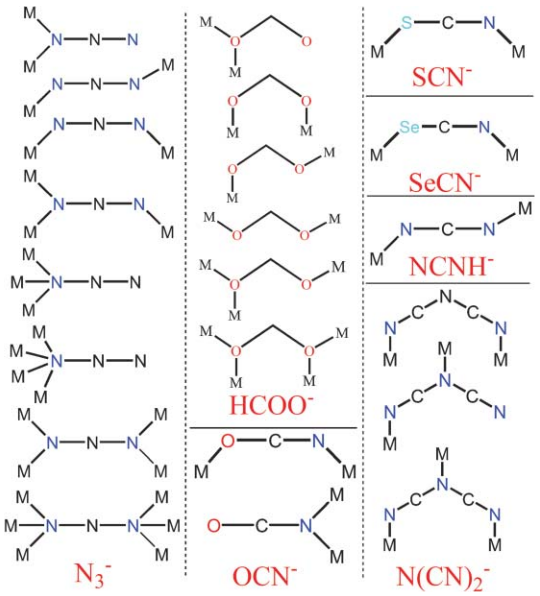
conjugated the bridges are, the more efficient the transmitted magnetic coupling will be. Thus, metal oxides with the oxygen atom as a single-atom bridge and cyanide-bridged molecular magnets, including some room-temperature molecular magnets, present two of the most widely explored and broadly used magnetic systems.[8] Although they are efficient for magnetic coupling, short bridges are somewhat lacking on the diversity of bridging modes. In opposite, magnetic coupling between two spins through a long pathway, especially longer than four single bonds, is thought to be very weak. Long bridges for magnetic systems are always conjugated in some form, such as oxalate,[9] pyrazine,[10] and TCNE.[11] Three-atom bridges, such as azido (N_3^-), formato ($HCOO^-$), thiocyanato (SCN^-) and hydrogencyanamido ($NCNH^-$), lie in the middle and justify themselves as good candidates to construct molecular magnets. These three-atom bridges are particularly well-suited in several aspects. First, they are not too long for magnetic coupling and can always transfer moderate or strong magnetic interaction, ferromagnetic (*FO*) or antiferromagnetic (*AF*). Second, as shown below, they show very rich and varied coordination characteristics and bridging modes to transition metal centers, which makes them capable to construct various interesting structures with efficient magnetic interactions. This will dramatically benefit the discovery of new molecular magnetic materials. Third, these three-atom bridges have an important feature, more or less in common, namely, that they will usually preclude the inversion center between the two bridged metal ions. This aspect is proved to be quite important in many systems because it will symmetrically allow the antisymmetric interaction (Dzyaloshinsky–Moriya interaction, DM), which has the Hamiltonian $H = -\boldsymbol{D}_{ij}\cdot[S_i \times S_j]$ with $\boldsymbol{D}_{ij}$ being the DM vector.[1a–c,12] This interaction acts to cant the spins because the coupling energy is minimized when the two adjacent spins are perpendicular to each other. The DM interaction requires the lack of the inversion center between the two relating spins. Thus, canted antiferromagnetism or so-called weak-ferromagnetism (*WF*) can be reasonably anticipated for many three-atom bridged compounds; and this is what we actually observed.

This article will mainly concentrate on those three-atom bridged magnetic systems we have explored, to demonstrate the design strategy, the various complexes and their rich magnetic properties. The characteristics of the three-atom bridges in coordination and magnetic transmitting and the role of the co-ligands and template will first be briefly discussed, followed by the main results obtained in our lab, from zero- to three-dimensional (0D to 3D) materials.

2 Coordination characteristics of the three-atom bridges and their roles in mediating magnetic interaction

We briefly summarize here the coordination characteristics of some three-atom bridges we have used (N_3^-, $HCOO^-$, SCN^- and $NCNH^-$) and their roles in mediating magnetic interaction. Considering the bridging part only, some ligands, such as 1,3-dca (dicyanamide), can also be viewed as three-atom bridges. Reviews of the detailed coordination chemistry of these bridges can be found elsewhere.



Scheme 1 The three-atom and three-atom-like bridges (N_3^-, $HCOO^-$, OCN^-, SCN^-, $SeCN^-$, $NCNH^-$, $N(CN)_2^-$) and their main bridging modes.

2.1 Azido (N_3^-)[13]

As one of the most versatile ligands, azido was used for the construction of enormous magnetic systems. Different types of bridging modes of azido, such as the 2.20 (end-on, *EO*), 2.11 (end-to-end, *EE*), 3.21, 3.30, 4.40 or even 6.33 as depicted in Scheme 1, can be found in actual compounds (for the Harris notation 2.20, 2.21, *etc*., please see ref. 14). Depending on these bridging modes, the azido can efficiently transmit different magnetic interactions. Generally, the *EE* azido is responsible for the *AF* coupling and *EO* azido for the *FO* coupling. Of course, the magnetic coupling also depends on the detailed coordination geometries, such as the $M–N_{azido}–M$ angles and the dihedral angle between the mean planes M–N–N–N and N–N–N–M′. The rich bridging modes and the ability to transfer different magnetic couplings lead to abundant magnetic behaviors, such as ferromagnetism, antiferromagnetism, ferrimagnetism, weak-ferromagnetism, spin-flop, single-molecule magnets, and single-chain magnets, observed in the azido-bridged systems. The investigation on the azido-bridged systems has been the focus of many researchers. Numerous interesting compounds have been reported and the structures and magnetism of Mn^{2+} and Ni^{2+} coordination complexes were well reviewed. Surprisingly, investigations for Co^{2+} remained nearly absent up to our work, which provides us a good opportunity to explore the $Co^{2+}–N_3^-$ system, in addition to other Mn^{2+} and Ni^{2+} systems.

2.2 Formato ($HCOO^-$)[15–18]

Since the hydrogen atom is not coordinated or involved in magnetic coupling, formato is actually a three-atom bridge. It has been observed to display multiple bridging modes, 2.20, 2.11, 3.21 and 4.22, to link two or more transition-metal ions forming various complexes (Scheme 1). Depending on the geometries of the formato bridge (*syn-syn*, *anti-anti* or *syn-anti*), it can mediate *FO* or *AF* coupling in different situations.

Interestingly, all of its bridging modes can find their corresponding analog in azido-bridged systems and transfer similar magnetic coupling. For example, both with the 2.11 mode usually mediate *AF* coupling. These considerable similarities may lead to compounds with similar structures and magnetic properties. Meanwhile, due to the differences in coordinating atoms (O or N), electronic structures (degree of conjugation), and the geometric characteristics (bent or linear) of azido and formato, the resulting structures and the magnetic properties can be very different. Although there are many formato-bridged compounds reported, the magnetic studies in this area are strangely lacking. Before our systematic investigation, the long-range ordered systems bridged by formato include the following examples: $[M(HCOO)_2(L)_2]$ (M = Mn, Fe, Co, Ni, Cu, L = H_2O, $HCONH_2$, $(NH_2)_2CO$),[16] dehydrates $[M(HCOO)_2]$,[17] and $[Mn(HCOO)_3]\cdot$Guest.[18] As we demonstrate in this article, many interesting results can be achieved in the metal–formate system.

2.3 Cyanato, thiocyanato and selenocyanato (XCN^-, X = O, S and Se)[19–22]

Although we will present only two SCN^--bridged examples in this article, the coordination chemistry and their roles on magnetic coupling of these pseudohalides are briefly summarized here for general interest. Due to their two different donor atoms (O/S/Se and N), they have less versatility and are less efficient as a magnetic coupler. Compared with azido, there are much fewer reports on the divalent first-row transition metal complexes bridged by them; and most of them are paramagnets above 2 K. Fully studied complexes are mainly compounds of Ni^{2+} and Cu^{2+}.[19,20] For OCN^- bridged Co^{2+} compounds, the first structurally characterized example[21] was reported in 2001. A similar situation stands for the SCN^- and $SeCN^-$. The 2D compounds $[M(SCN)_2(ROH)_2]$ (M = Mn^{2+}, Co^{2+}; R = CH_3, C_2H_5, C_3H_7) and the proposed 1D chain $[M(SCN)_2$(2,2-bipyridine)] (M = Mn^{2+}, Co^{2+})[22] are the rare examples investigated thoroughly for SCN^-. For $SeCN^-$, no example of Mn^{2+} and Co^{2+} can be found in the Cambridge Structural Database (version released June 2007). According to the existing structures, all of them can act as *EE* bridges and transmit weak magnetic interaction. Actually, the SCN^- and $SeCN^-$ adopt the *EE* mode in most cases. The M–N–C and M–X–C angles and M–XCN–M dihedral angle influence the sign of the magnetic coupling greatly.[20a] The existing data suggest that the *EE* OCN^- and SCN^-can transmit both *AF* and *F* coupling while the $SeCN^-$ transmits mainly the ferromagnetic coupling. As for the *EO* mode, the existing examples are mainly for the OCN^- (using N atoms exclusively) with Ni^{2+} and Cu^{2+} ions. The magnetic coupling transmitted by *EO* OCN^- is generally weak, with the signs depending on the M–N–M angle.

2.4 Hydrogencyanamido ($NCNH^-$)[23]

The $NCNH^-$ is one of the two basic forms of the cyanamide ($NCNH_2$). Although it is believed that coordination polymers bridged by $NCNH^-$ should exist with regard to the well-characterized polymers bridged by its isoelectronic species azido, the coordination chemistry and the ability of $NCNH^-$ to mediate magnetic coupling remained almost unexplored. Only three $NCNH^-$ bridged coordination complexes have been reported before we started to explore this interesting ligand. Although there are not enough examples to draw a conclusion on the magnetic interactions transferred by $NCNH^-$, there is a widely investigated analog of $NCNH^-$: the dca ($N(CN)_2^-$) anion, especially in μ-1,3 bridging mode, which was found to provide strong coupling between metal ions. These aspects inspired us to explore $NCNH^-$ as a bridging ligand to construct the molecular magnets.

2.5 Three-atom-like bridge dicyanamido ($N(CN)_2^-$)[24]

Many bridges, which are not three-atom ligands themselves, can act as three-atom bridges. Most of them use part of the ligand (three atoms involved) to bridge the metal centers and the bridging part dominates the magnetic properties. From this point of view, the carboxylate-bridged complexes, in addition to the formate, can actually be classed as such and represent a huge catalogue of compounds. In this article, we will only describe the dicyanamido ligand. Although there are a variety of bridging modes for dca, we will focus our attention on the μ-1,3 bridging mode. This bridging mode can effectively mediate the magnetic coupling, mostly *AF*, and justifies itself as a good candidate to construct molecular magnets. Several examples with dca as bridges will be discussed later. For a comprehensive view, the readers are directed to other papers.

3 Co-ligands, templating cations and other short bridges

Although magnetic coordination polymers could be constructed by only the metal ions and the bridging ligands, many other components could be involved. Depending on their roles, these components can be divided into two categories: co-ligands and templates. The co-ligand is an ancillary ligand, usually an organic molecule coordinating to the metal; while the template, being neutral or charged, and of specific size and shape, does not coordinate but requires specific space and interactions in the resulting structure. Both of them are very important to the formation of some particular architecture and to the structure modification, whether they are favorable to the magnetic interaction or not.

3.1 Co-ligands[25,26]

The co-ligands can be either terminal (*endo*) or bridging (*exo*). The terminal co-ligands will always block the metal's available coordination sites and decrease the possibility to form higher dimensional structures. Magnetically, they are normally adverse to the purpose of achieving high T_C magnets. However, they make it easier to obtain low-dimensional magnetic materials. Isolated clusters like SMM, 1D magnetic chains like SCM, and 2D magnetically anisotropic layers are common results when some terminal co-ligands are structurally included. Due to the recent ongoing interests in low-dimensional magnetic systems, the terminal co-ligands have been reinvestigated extensively these days. In our three-atom bridged systems, these terminal co-ligands also play very important roles.

The bridging co-ligands are also very important for our study. Considering their ability to transfer magnetic interactions, they can be divided into two groups: magnetically active and inactive. The former co-ligands, such as pyrazine and N-oxidized pyrazine, not only can influence the structures of the complexes, but also can directly modify the magnetic properties. On the other hand, the magnetic inactive bridges, which are actually most of the cases, are usually long ditopic organic compounds. Their roles lie mainly on the structural modulation, and they can subtly adjust the magnetic property of the materials by modifying the weaker magnetic interaction, such as interchain or interlayer exchange. Furthermore, the bridging co-ligands can be either rigid or flexible. For the rigid co-ligands, prediction of the resulting structures is sometimes possible although it is very difficult in most cases. On the contrary, the conformational flexibility of the flexible co-ligands adds another freedom and may induce a variety of structures, such as the formation of the supramolecular isomers.

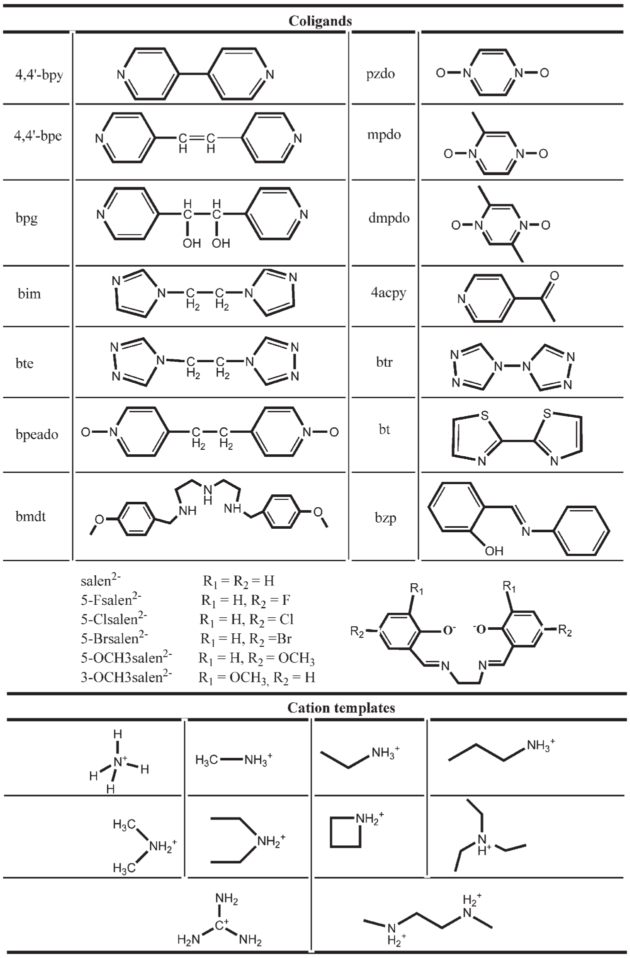
3.2 Templating cations

Templated synthesis is of great importance in modern chemistry. It has naturally been employed in the syntheses of many magnetic systems, such as oxalates, azides and dicyanamides. While co-ligands can be of templating effect to some extent, cations (or anions) can act as templates to guide the formation of anionic (cationic) metal–organic frameworks with special structures and magnetism. Ammonium cations are perhaps the most popular templates in synthesizing systems such as artificial zeolites,[27] metal phosphates,[28] polyoxometalates,[25] mesoporous MCM-41 materials,[29] and metal oxalates.[30] The template effects of ammonium cation lie in (i) the formation of hydrogen bonds between the cation and the templated components, (ii) imprinting – the transfer of the structural information (size and shape) of the cation onto the templated architecture, and (iii) charge-compensation. These effects guide and bring the building blocks (metal ions and ligands) together to form the templated assemblies. Recently we have employed this approach to magnetic frameworks of metal formates, metal azides, *etc.*, and interesting results in both structural and magnetic respects have been obtained.

Listed in Scheme 2 are the main co-ligands and template cations incorporated in our three-atom-bridged systems. Whether they are terminal or bridging, magnetically active or inactive, rigid or flexible, big or small, they lead to great success for our study, especially for the preparation of low-dimensional magnetic systems.

3.3 Mixed short ligands

The above-mentioned short bridges, being the effective magnetic mediators, have formed several of the most important families of molecular magnets. However, combining two or more types of these short bridges in one material is still a challenge and of great interest for the rational design and construction of new molecular magnets with special structures and interesting properties in the view of exploiting their individual advantages of both coordination and magnetism. Several attempts have been made at combining oxalate and azide bridges, or cyanide and oxalate bridges. We demonstrate that, by carefully selecting suitable building blocks, it is possible to prepare new hybrid magnetic materials containing, cyanide and azide, azide and carboxylates, *etc.*



Scheme 2 The schematic structures of the co-ligands (bridging or terminal) and template cations used in our work.

4 Magnetic molecular solids based on three-atom bridges

With the above mentioned three-atom bridges, co-ligands, and templates, we successfully synthesized many interesting magnetic molecular solids. Some of them will be briefly described, from low to high dimensionality. As for the dimensionality, we refer only to the part bridged by the three-atom bridges, thus it regards the dimensionality of strong magnetic interactions *via* these short bridges. The whole framework can be of higher structural dimensionality when the connection by the bridging co-ligand is considered. No attempt is tried to describe exhaustively the complexes bridged by these bridges. Our attention here is focused on our own results together with some closely related systems.

4.1 Single-molecule magnets and single-chain magnets

These two amazing systems behave like real magnets but with slow magnetic relaxation and quantum effects. For this reason, SMMs and SCMs have attracted much attention ever since their discovery.[5,6] This prompted us to synthesize such compounds using our three-atom bridges and synthetic strategies. The conditions to get a SMM or SCM are very critical. First of all, an overall easy axis (Ising) type magnetic anisotropy is definitely required for both. Although no causality exists between the anisotropy of an individual spin and the whole cluster/chain, it is still preferred to try the Ising type metal ions, like Co^{2+} and Ni^{2+} in our cases. Second, a ground state with a large spin and a strong intra-molecular magnetic interaction are needed to increase the energy barrier or blocking temperature. These strongly depend upon the bridges between the spins. For all bridges mentioned above, we focused on azido since it might transfer the strong magnetic interaction, *FO* or *AF*, and lead to high residual moments arising from ferro-, ferri- or even weak-ferromagnetic states. Furthermore, to avoid 3D long-range ordering, the inter-cluster/interchain interactions need to be very weak. For this purpose, terminal co-ligands and also long bridging co-ligands can be used to isolate the clusters and the chains. Considering these aspects, several SMM and SCMs were obtained.

With the terminal chelating co-ligand bzp, a disk-like heptanuclear cluster $[Co_7(bzp)_6(N_3)_9(CH_3O)_3](ClO_4)_2(H_2O)_2$ (**1**) can be synthesized (Fig. 1).[31] The azido ligands adopt *EO* mode to bridge Co^{2+} centers and transmit efficient *FO* interaction. The structure is represented by a closest-packing arrangement of donor N/O and Co atoms with a local S_6 symmetry. As expected, the bulky bzp capping every Co^{2+} center sufficiently isolates the Co_7 disks away from each other. The *FO* interactions lead to the ground state to be $S_T = 7/2$ (efficient $S = 1/2$ for Co^{2+} at low temperature) and slow relaxation at both zero and non-zero dc fields were observed. However, micro-SQUID measurements on the single crystal revealed a thin hysteresis and suggested that **1** is not a real SMM. The main reasons are likely to be the significant spin–orbit interaction and the rhombic ZFS parameter *E*.

The use of another terminal co-ligand bt, also chelating, gave the infinite chain compound $[Co(N_3)_2(bt)]$ (**2**) with double *EO* azido bridges (Fig. 2).[32] The bulky co-ligand keeps the helix chains isolated. As expected, the *EO* azido transmits strong *FO* interactions along the chain and the interchain coupling is small enough to prevent **2** from long-range ordering. Slow magnetization relaxation and hysteresis effects confirmed the SCM behavior of **2** with a blocking temperature of 5 K and the energy barrier of 90 K. It is worth noting that compound **2** is the first SCM with homospins.[6]

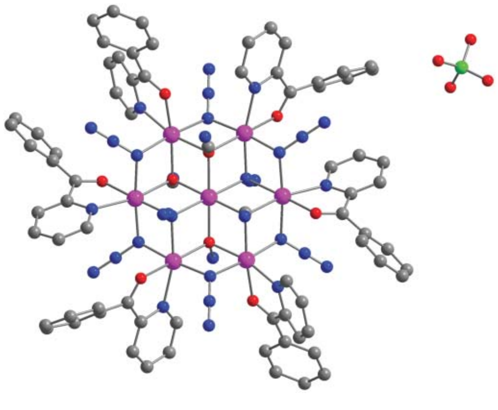


Fig. 1 The azido-bridged heptanuclear Co_7 structure of **1**.

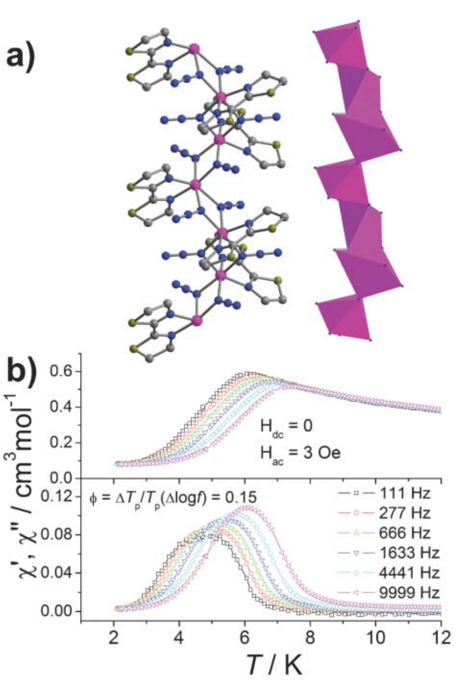


Fig. 2 (a) The helix chain of **2** with Co^{2+} bridged by EO azido, and (b) the ac susceptibility of **2** under zero dc field showing strong frequency dependence.

Being confident of the *EO* azido bridged Co^{2+} chains to be SCMs, provided the small enough interchain interaction, we turned to another approach to generate isolated 1D Co^{2+} chain by using a long co-ligand. This was proved to be successful for compound **3** with the formula $[Co(N_3)_2(H_2O)_2]$-(bpeado) where the 1D Co^{2+}–N_3^- chains are isolated by bpeado (Fig. 3).[33] The connections between the Co^{2+} ions in **3**

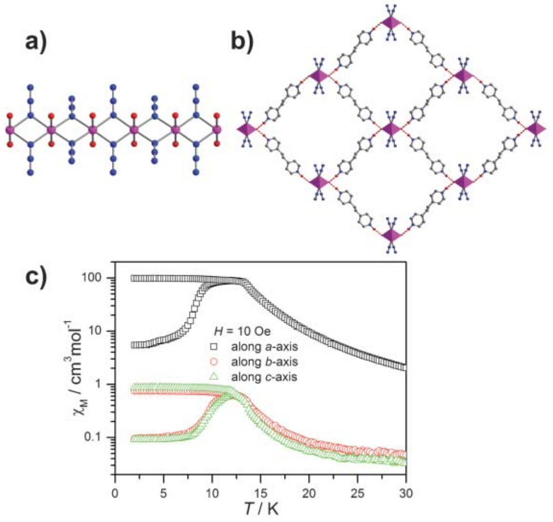


Fig. 3 (a) The 1D cobalt–azido chain of **3**; (b) the interchain relationship with bpeado hydrogen bonding to the coordination water of Co^{2+} and isolating the chains; (c) the ZFC/FC curves for **3** under 10 Oe along three different crystallographic axes, showing the Ising type anisotropy.

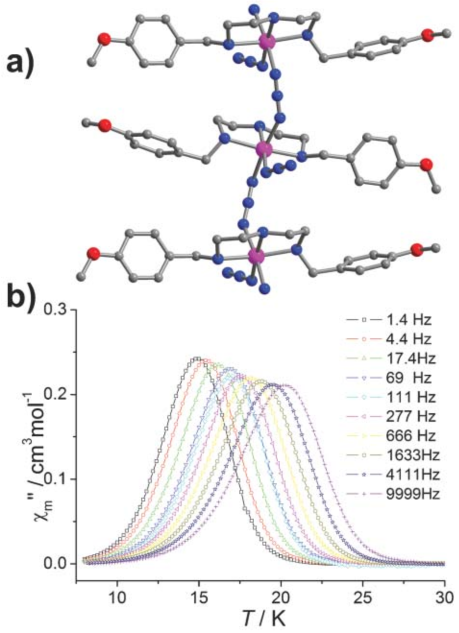


Fig. 4 (a) The 1D Ni^{2+} chain bridged by *EE* azido of **4**, the bmdt ligands separate the chains to each other; (b) the out-of-phase part of the ac susceptibility under zero dc field.

are also double *EO* azido linkages as in **2**. In contrast, **3** has only one unique Co^{2+} center and the chain is perfectly straight. The bpeado, not acting as a ligand, is H-bonded to the coordinated water and separates the chains well, with an interchain distance larger than 10 Å. Magnetic measurements both on the powder and on a single crystal of **3** show very interesting magnetic properties, including strong Ising-type magnetic anisotropy, slow magnetization relaxation, and very large hysteresis loops.

All examples above use the *EO* azido to construct the SMM and SCMs because of its contribution of *FO* interaction. However, the *AF*-favored *EE* azido can also serve as a good bridge for SCM and SMM purposes. Specifically, spin canting due to this three-atom bridge can lead to a weak-ferromagnetic ground state in certain conditions, which will also generate large magnetization in an infinite chain and lead to SCM behavior if other conditions are fulfilled.[6,34] This is the case for the compound $[Ni(\mu\text{-}N_3)(bmdt)(N_3)](DMF)$ (**4**) (Fig. 4).[35] The Ni^{2+} ions were connected by a single *EE* azido to form a 1D chain, while the big bmdt helps to well separate the chains in space (>9.5 Å). Magnetic measurements revealed the strong *AF* interaction between Ni^{2+} and SCM like behaviors such as the slow magnetization relaxation and big hysteresis loops below the blocking temperature of 15 K. However, more study is needed to fully understand the relaxation behavior of **4** since it can not be simply interpreted by Glauber dynamics as a typical SCM.[6,36]

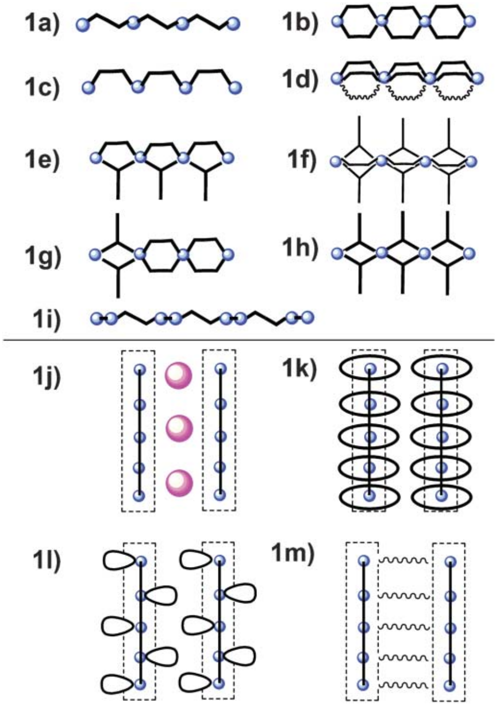
4.2 Low-dimensional molecular magnetic systems

As demonstrated above, by using terminal or long bridging co-ligands, discrete clusters and chains which behave as SMM and SCM materials can be achieved successfully. Due to the rigorous conditions necessary for the SCMs, most of the 1D chains we obtained do not behave as SCMs. Because they are easier to analyze theoretically, these chains offered us good model systems to study the magneto-structural correlations and other magnetic phenomena.

4.2.1 Magnetic chains bridged by three-atom bridges. Depicted in Scheme 3 are some chain topologies and interchain relations we observed (for compound **2**: 1h + 1l; **3**: 1h + 1m, **4**: 1a + 1k). We are not trying to cover all the possible topologies observed so far. For other 1D topologies, the readers can refer to other reviews for details.[8*b*,37]

Since azido-bridged chain compounds are quite versatile,[38] we will only focus on some of our results. When the co-ligand bzp was involved in the Cu^{2+}/N_3^- system, two structurally related exotic 1D tapes with serial and parallel cyclic eight-member copper rings were obtained successfully in different solvent systems: $[Cu_4(N_3)_8(CH_3CN)_3(bzp)_2]$ (**5**) and $[Cu_5(N_3)_{10}(bzp)_2]$ (**6**) (Fig. 5).[39] All azido are of *EO* modes (2.20 and 3.30) to bridge the Cu^{2+}. Magnetically, both of them remain paramagnetic down to 2 K. By analyzing the susceptibility data and broken-symmetry DFT calculation, the *EO* azido ligands are found to transmit *FO* coupling in **5** and both *AF* and *FO* coupling in **6**. The nature of the magnetic interaction coupled by *EO* azido was found to be dependent on the Cu–N–Cu angle, the dihedral angle between two basal planes of copper, and also the distortion of the coordination geometry of Cu^{2+}.

Besides the SCM compounds **2** and **3**, a series of azido bridged 1D compounds can also be constructed with long



Scheme 3 The schematic 1D chains (1a–1j) bridged by the three-atom bridges; the solid lines represent three-atom bridges and the wavy line the co-ligands. The chains are separated from each other either by a bulky counter ion/solvent (1j), a big terminal ligand (1k and 1l), or a long bridging ligand (1m).

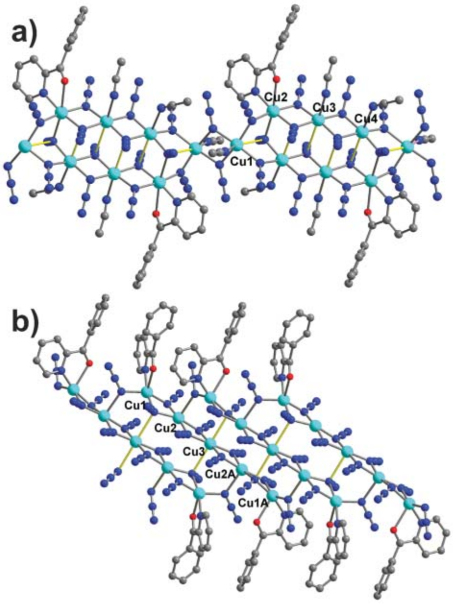


Fig. 5 The 1D tapes of **5** (a) and **6** (b) with Cu^{2+} bridged by azido.

bridging co-ligands. $[Mn(N_3)_2(H_2O)_2](bpeado)]$ (**7**)[33] and $[Mn(N_3)_2(bim)]$ (**8**)[40] with co-ligand bpeado and bim having the same chain type (1h). Compound **7** is isostructural to **3** with bpeado H-bonding to the coordinated water, while bim in **8** coordinates to Mn^{2+} and further connects the $[Mn(N_3)_2]_n$ chains into a distorted 3D diamondoid structure. Interestingly, although **7** and **8** have the same type of $[Mn(N_3)_2]_n$ chain, their magnetic properties are totally different. **7** remains paramagnetic above 2 K with the *AF* interaction; while in **8** the magnetic exchange is *FO* and it has a field induced spin-flop and a metamagnetic transition below T_C = 3.0 K. This difference should arise from the angle of $Mn–N_{azido}–Mn$: 99.9° in **7** and 103/106° in **8**.[13] These two examples show us the importance of the co-ligands in the modification of the three-atom bridged magnets.

Using formato and 4,4′-bpy, two isostructural compounds $[M(CHOO)_2(bpy)](H_2O)_5$ (M = Co (**9**), Ni (**10**)) with isolated chains of type 1c + 1m bridged by 2.11-*anti-anti* formato were constructed.[41] They have the 3D uninterpenetrated $CdSO_4$ framework with channels filled by water. Moderate *AF* coupling was observed and **9** is an antiferromagnet below 3.0 K, while **10** is a weak-ferromagnet below 20 K.

Since both azido and formato show excellent performances in constructing new magnetic materials, the combination of them in one system should also be of interest. In this respect, two new compounds were synthesized $[(CH_3)_2NH_2][M(N_3)_2(HCOO)]$ (M = Fe (**11**), Co (**12**)), consisting of chains of $[M(N_3)_2(HCOO)^-]_n$ (type 1f + 1j) isolated by the $[(CH_3)_2NH_2]^+$ cation.[42] They are good examples of obtaining isolated 1D chains by using counter ions. Below about 10 K metamagnetism arising from the *AF* coupled ferromagnetic chain was observed for both of them. Replacement of the $[(CH_3)_2NH_2]^+$ by other bulky diamagnetic cations might decrease the interchain interaction further and result in the better isolation of the ferromagnetic chains, which is required for the construction of SCMs.

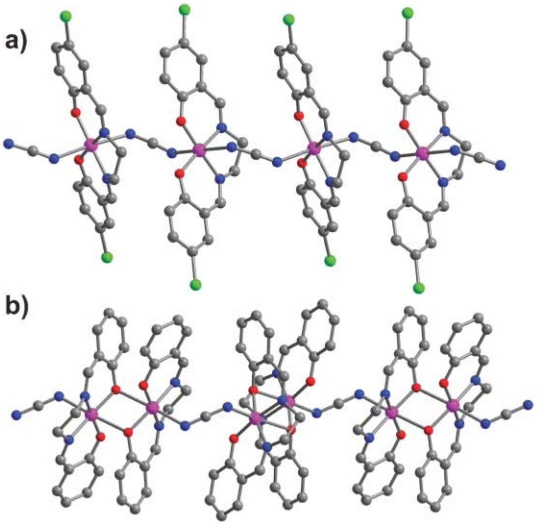


Fig. 6 The typical Mn^{3+} chains bridged by $NCNH^-$ with the repeating unit mononuclear [Mn(L)] (a) or binuclear $[Mn_2(L)_2]$ (b).

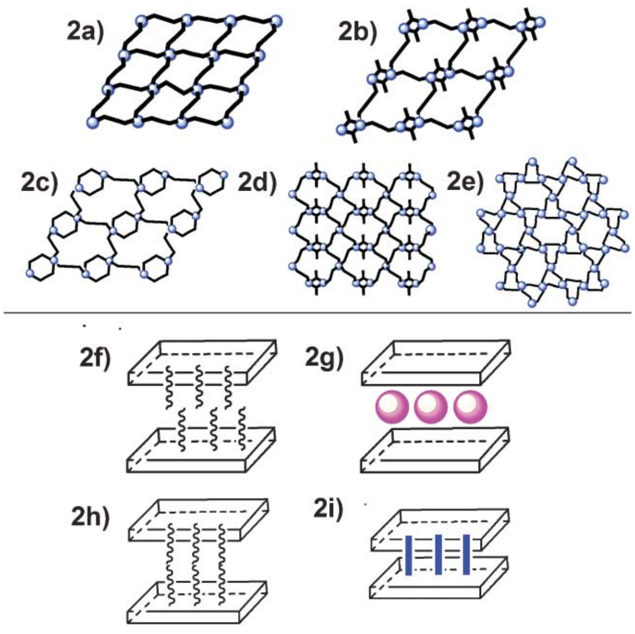
For SCN^- and some flexible bridging co-ligands, we also get two SCN^- bridged cobalt chains: $[Co(SCN)_2(bim)]$ (**13**) and $[Co(SCN)_2(bte)]$ (**14**).[40] **13** is a triple-bridging chain of type 1d + 1k with double *EE* SCN^- and one bim as a bridge; and **14** contains 1D chains with double *EE* SCN^- and these chains are further extended to (4,4) layers by the *anti*-bte (type 1b + 1m). The *EE* SCN^- was found to transmit weak *FO* interaction between the cobalt ions.

By introducing various tetradentate Schiff base co-ligands (salen and its derivatives) into the $NCNH^-$ system, a series of chain compounds with Mn^{3+} bridged by $NCNH^-$ were obtained.[43] In these complexes, the resonance structure of $N{\equiv}C–NH^-$ dominates the bonding mode of the $NCNH^-$ ligand. Adopting the *EE* mode, the $NCNH^-$ ligand bridges the mononuclear [Mn(L)] units or the dinuclear $[Mn_2(L)_2]$ units to form the 1D chains of type 1a and 1i (Fig. 6). The asymmetric bridge of $NCNH^-$ was found to transmit *AF* interactions between Mn^{3+} ions (*J* is in the range of -0.6 to -1.2 cm^{-1}). The asymmetric character of $NCNH^-$ induces the establishment of spin-canting in these chains. Depending on the sign and strength of the interchain coupling, paramagnetism, weak-ferromagnetism or metamagnetism were observed for these chains at low temperatures.

4.2.2 2D layers bridged by three-atom bridges.

The introduction of the co-ligands to the three-atom bridged magnetic systems can also generate some 2D layers. Depicted in Scheme 4 are the main topologies of the three-atom bridged 2D layers we obtained, together with the interlayer relationships. Most of these 2D compounds show long-range magnetic ordering, providing the layers are not too far from each other.

For the azido bridged systems, layers of type 2a–2d had been reported before we started our research.[13,44] However, most of the examples concerned only Mn^{2+} and Ni^{2+} ions. For Co^{2+}, the existing examples were quite rare. Therefore, we focused our attention mainly on the cobalt systems, together with some Mn and Ni systems along with some new co-ligands.



Scheme 4 The schematic 2D layers (2a–2e) and interlayer relationship (2f–2i). The layers can be separated by terminal co-ligands (2f), bulky counter ions (2g) and bridging co-ligands (2h and 2i). The bridging co-ligand can be either magnetically inactive (2h) or active (2i).

For the Mn–azido system, a series of compounds with the layer of type 2a with *EE*-azido can be obtained with different co-ligands: the terminal ligand btr ([Mn$(N_3)_2$(btr$)_2$], **15**),[45] the magnetic inactive bridging ligand bpg ([Mn$(N_3)_2$(bpg)], **16**),[46] and the magnetic active bridging ligand pzdo ([Mn$(N_3)_2$-(pzdo)],[47] **17**) (Fig. 7). The basic structural characteristics of the (4,4) layer is similar to each other and also to some reported examples.[13,48] *AF* coupling through *EE* azido was found for all of them although the magnitude differs slightly due to some subtle differences in the details of the bridging geometries. However, their interlayer connections are significantly different. For **15**, the adjacent layers are connected to each other by weak CH···N hydrogen bonds where the shortest interlayer Mn···Mn distance is 12.4 Å (2f). For **16**, although the layers are covalently connected, the interlayer Mn–Mn distance is even longer (13.8 Å) due to the long ligand bpg (2h). As for **17**, the shortest interlayer Mn···Mn distance is about 6 Å (2i). Furthermore, as our results show, pzdo can transmit the moderate magnetic exchange,[47,49] leading to the higher T_C of **17**. Magnetic investigations revealed the critical temperatures for **15**, **16** and **17** as 23.7, 10.8 and 62 K, respectively. In **15** and **16**, the *AF* coupled Mn^{2+} spins cant to each other resulting the *WF* states. In fact, spin canting is quite common in these 2D azido-bridged systems and should be directly related to the non-centrosymmetric character of the *EE* azido. Interestingly, detailed magnetic measurements on the single crystal of **15** revealed the coexistence of hidden spin-canting, metamagnetism, and spin-flop. Magnetic phase diagrams in both the T–H^{a^*} and the T–H^b planes were determined (Fig. 8) and possible spin configurations before and after the phase transitions were proposed. The interlayer coupling, despite its weakness compared to the intralayer coupling through azido, plays a very important role in its magnetic behavior. For **17** with layers pillared by pzdo, the efficient coupling between the layers remarkably increases the T_N up to 62 K, which is proved by the magnetic measurements and powder neutron diffraction on the fully deuterated sample. In fact, **17** is a three-dimensional system regarding the magnetic interactions along the three dimensionalities. This whole series of results demonstrates clearly the importance of the co-ligands in the three-atom bridged magnetic materials.

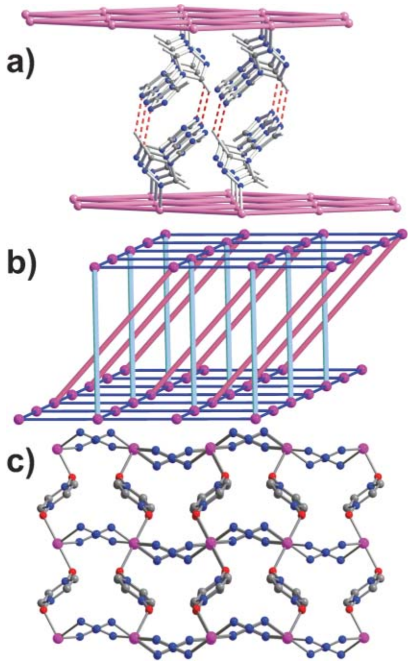


Fig. 7 The 3D structures of **15** (a), **16** (b) and **17** (c) showing different interlayer relations with similar Mn^{2+} (4,4) layers bridged by *EE* azido.

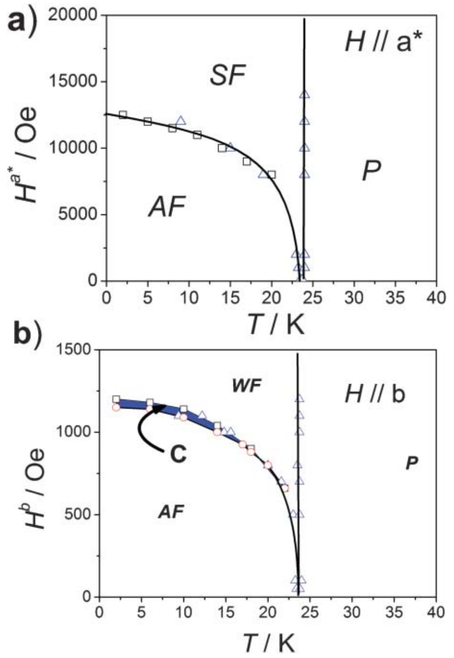


Fig. 8 The magnetic phase diagrams of **15** in both the T–H^{a^*} (a) and the T–H^b (b) planes.

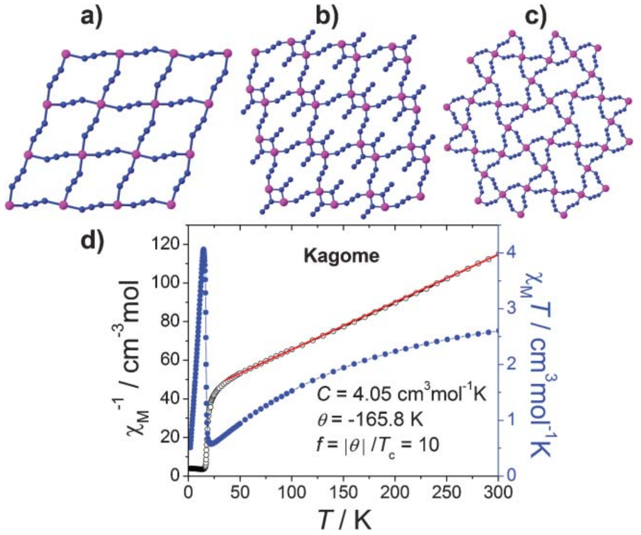


Fig. 9 The azido bridged Co^{2+} layers of **18** (a) **19** (b) and **20** (c) with the topology of square, honeycomb and Kagomé; (d) The temperature dependent inverse susceptibility of **20** showing the strong spin frustration.

Besides the ability to modify the structures, they can influence the magnetic properties greatly, not only by means of generating new structures and adjusting the interlayer distances to modify the magnetic interactions indirectly, but also by participating in the magnetic coupling directly.

Similar and even more interesting are the less investigated 2D Co^{2+}–azido system. For Co^{2+}, another important issue, the strong anisotropy deserves much more attention because it will generally lead to the WF state with remarkable spin-canting, together with the DM interaction. With bpg as a co-ligand, a series of Co^{2+}-azido layers of type 2a, 2b and 2e with the formula $[Co(N_3)_2(bpg)](S)_n$ (**18**, S = nothing; **19**, S = DMSO, n = 1; **20**, S = DMF, n = 4/3) were successfully obtained by simply using different solvents during the syntheses (Fig. 9).[50] The bpg links the 2D layer to form the pillared layer architectures (2h). DMSO and DMF are crucial for the generation of **19** and **20** since various H-bonds exist between the OH groups in bpg and the guest molecules. For **19**, the topology can be considered as the same as **18** if the *EO*-N_3^- bridged $[Co_2]$ dimer is considered as one node. The layer of **20**, a Kagomé lattice, was constructed by corner sharing triangles and was interesting due to its possible geometrical frustration.[51] Significant *AF* exchange is transmitted through the *EE* azido for **18–20**. As mentioned above, no inversion centers exist in the middle of the adjacent *AF* coupled Co^{2+} centers ($[Co_2]$ for **19**) although these compounds all belong to centrosymmetric space groups. As expected, all of them are weak ferromagnets below T_C. The rare molecule-based Kagomé compound **20** shows strong spin frustration, as revealed by the large f ($f = |\theta|/T_C = 10$) parameter,[51] and re-enters into a spin glass state at low temperature.

As far as future applications, molecular magnets with large and permanent spontaneous magnetization below T_C are continuing to be pursued. However, because the *FO* coupling is not as common and strong as the *AF* coupling, designs of the ferromagnets are limited. Other approaches to this target should be explored. As a substitute, ferrimagnets with large magnetization, arising from the uncompensated magnetization of two magnetic lattices, have attracted much attention.[1c,52] Most of the synthesized high T_C Prussian Blue magnets are actually ferrimagnets.[3b,c,8a,e] On the other hand, compound **19** shows the hint of another efficient approach to obtain strong magnetization magnets using *AF* interaction. We call it a weak-ferromagnetic approach. Although numerous molecular weak-ferromagnets were reported, these investigations stayed mainly on the theoretical level since most of them have small canting angles and thus small spontaneous magnetization. However, as long as the canting is efficient, large magnetization can also be generated.[24c,26c,53,54] For example, when the canting angle is 20°, the resulting net moment could be 34.2% (sin 20°) of the total. This is even more efficient than the ferrimagnetic alignment of two heterospins with S and $2S$ (the net moment is S, 33.3% of the total $3S$). For example, the canting angle is 5.2° in **19**, resulting in about a 10% residue of the spin. As a mater of fact, in another compound also with the (4,4) layer of Co^{2+} bridged by *EE* azido, the canting angle can reach even larger values.[54] Among the reported molecular weak-ferromagnets, those with big canting angles are quite rare.[24c,26c,53] Interestingly, all these examples have two important common aspects: strong anisotropic spins and the three-atom bridges.

In the above-mentioned azido compound **15**, the spin-flop transition happened under external field parallel to the spin. However, due to the strong *AF* coupling between Mn^{2+} transmitted by N_3^-, the critical field H_C (defined as the field transferring the spin-flop state to a totally saturated state)[1a] is too high to achieve experimentally. Considering the similarity and difference of azido and formato, 2D layers of Mn^{2+} bridged by $HCOO^-$ may have the similar spin-flop transition and the H_C might be remarkably lowered due to the weaker exchange through formato. This is the case in $[Mn_2(HCOO)_3(4,4'\text{-bpe})_3(H_2O)_2](H_2O)(ClO_4)$ (**21**),[55] which is also a pillared layer structure with Mn–HCOO herringbone (6,3) layers pillared by 4,4′-bpe, with a ClO_4^- anion and lattice 4,4′-bpe residing in between (Fig. 10(a) and (b)). Investigation on a single crystal revealed an antiferromagnet with spins all perpendicular to the layer below T_C = 2.5 K, and a spin-flop transition happened under an external field parallel to the spins (Fig. 10(c)). Due to the weaker interaction through $HCOO^-$, its T_C and H_C are both lower than **15**, falling in the measurement range of the SQUID system. Analysis of the data gives the detailed phase diagram and further intrinsic parameters. In addition, its magnetic properties, especially the critical field H_C can be finely tuned by anions with different sizes, like NO_3^-, Br^-, I^- and BF_4^-, which can be included by choosing different starting materials. Furthermore, the stack of the 4,4′-bpe in the lattice satisfies the Schmidt's geometric criterions for [2 + 2] photodimerization.[56] Upon exposure to the UV light, the lattice bpe molecules become photoactive to dimerize to tetrakis(4-pyridyl)cyclobutane. Although it is now difficult to study the influence of the photoreaction on its magnetic property, **21** provides a good example of the design of the multifunctional materials using functional co-ligands.

As for the dicyanamide (dca) system, the employment of co-ligands pzdo, mpdo and 2,5-dmpdo also works to give out

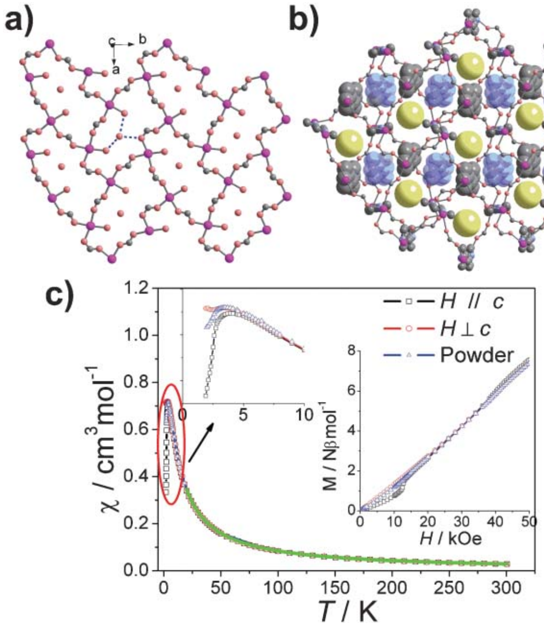


Fig. 10 (a) 2D herringbone layer of **21** with Mn^{2+} bridged by $HCOO^-$. (b) The pillared-layer structure, the big yellow balls are for the anion and the lattice bpe molecules are shown in blue, forming 1D columns along *b* with distances smaller than 4.2 Å. (c) The temperature dependent χ and field dependent magnetizations at 2 K for a single crystal ($H \parallel c$ and $H \perp c$) and a powder sample.

three layer compounds $[Co[N(CN)_2]_2(L)]$ (L = pzdo (**22**), mpdo (**23**) and 2,5-dmpdo (**24**)).[57] Both **22** and **23** contain similar 2D triangular layers with Co^{2+} bridged by the mixed 1,5-μ_2- and μ_3-dca (Fig. 11(a)). The pzdo and mpdo use one of the two N-oxido atoms to coordinate to cobalt and act as terminal ligands to separate the adjacent layers (type 2f). Owing to the μ_3-dca, long-range ferromagnetic ordering was observed for both **22** and **23** below *ca.* 2.5 K. Actually, this 2D network was also observed in another two compounds $[M(dca)_2(H_2O)](phenazine)$ (M = Co, Ni), where long-range order was observed in the Ni^{2+} complex.[57c] Similarly, the dca ligands in **24** use 1,5-μ_2 and 1,3-μ_2 modes to link Co^{2+} into a (4,4) layer (Fig. 11(b)). Interestingly, the co-ligand 2,5-dmpdo also acts as a bridge to pillar the 2D layers and as an intermediate for the magnetic exchange (type 2i). Thus T_C of **24** is increased to 10.8 K. Here, we can see the sensitivity of these systems because even a small change in the co-ligands can dramatically change the final structures and magnetic properties.

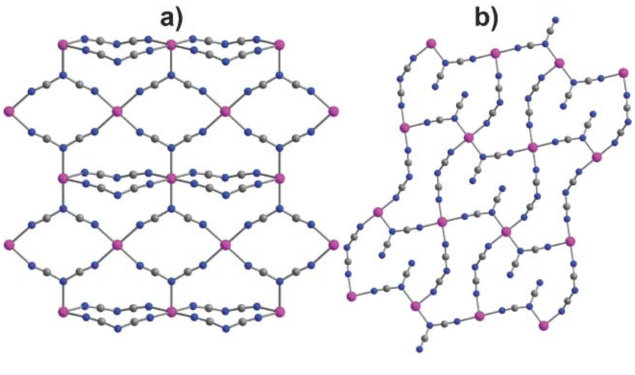


Fig. 11 The 2D layers bridged by dca of **22–23** (a) and **24** (b).

Similar to the idea of combining N_3^- and $HCOO^-$ into one system, the N_3^- can cooperate with another bridge, the CN^-, and gave some other interesting results. Including N_3^- to the CN^- bridged compound $[Cr(phen)(CN)_4]_2[Mn(H_2O)_2](H_2O)_4$ (**25**) extends the structure dimension and gives a 2D compound $Mn(N_3)(CH_3OH)[Cr(phen)(CN)_4](CH_3OH)$ (**26**).[58] All the N_3^- bridges are in the *EO* mode and responsible for *FO* coupling. With the structure increasing from 1D to 2D, the T_C also increases dramatically from 3.4 K for **25** to 21.8 K for **26**. This mixed-bridge approach is currently attractive for the cyanide system. Combination of the same system with other bridges such as oxalate and dca also leads to other new compounds with higher structural dimensionalities and other interesting aspects.[59,60] This lies out of the scope of this article and will not be discussed in details.

4.3 3D systems, weak-ferromagnets and porous magnets

As mentioned before, the structurally 3D systems we discuss here are also magnetically three-dimensional, and usually, the short bridging ligands link magnetic metal ions along three dimensionalities. Therefore, the magnetic interactions along the three dimensionalities in the materials are similar or comparable regarding their strength, and the materials usually show 3D long range magnetic ordering. The three-atom bridges we used are usually non-centrosymmetric bridges, satisfying the requirement for the DM interaction, this allows the occurrence of spin-canting or non-collinear spin-arrangement. We present here 3D metal–formates systems recently investigated.

The first two materials are $[M(HCOO)_2(4,4'\text{-bpy})]$ with M = Mn (**27**) and Co (**28**).[41] They are interesting mainly because they show both great similarity and difference between azido and formate. The two compounds are isostructural, showing a 3D diamondoid structure if the formates are considered as linkers only (Fig. 12). Interestingly, compound $[Mn(N_3)_2(4,4'\text{-bpy})]$ has a very similar structure except that the linkers are azido.[26a,b] Furthermore, due to the similar *AF* coupling transmitted through formato and azido and their non-centrosymmetric characters, **27**, **28**, and their azido analog all show weak-ferromagnetism below T_C. Of course, the critical temperature of **27** is significantly lower than that of $[Mn(N_3)_2(4,4'\text{-bpy})]$ because of the weaker coupling through $HCOO^-$. This similarity and difference of $HCOO^-$ and N_3^-, as is also revealed in the amine-templated metal–formate

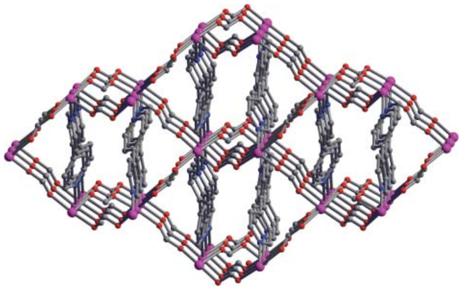


Fig. 12 The formate bridged diamondoid structure of **27** and **28**.

frameworks and their azido analog $[(CH_3)_4N][Mn(N_3)_3]$,[61] provided us a unique synthetic approach to these compounds.

The second series of materials we describe here are the metal–formate frameworks templated by cations of protonated amines.[62–65] Our systematic investigation demonstrated that these materials can be obtained by employing protonated amine cations of different sizes in non-coordinating solvent, and the outcome is dependent on the size and shape of the cations. The smallest ammonium NH_4^+ resulted in the chiral magnetic salts $[NH_4][M(HCOO)_3]$[62] though the starting materials are achiral. The structure is a framework with the rarely-observed $4^9{\cdot}6^6$ topology (Fig. 13(a)) consisting of octahedral metal centers connected by 2.11-*anti-anti* formato ions and the ammonium cation arrays located in the channels. In cases of the mid-sized monoammonium cations ($AmineH^+$) $CH_3NH_3^+$, $(CH_3)_2NH_2^+$, $CH_3CH_2NH_3^+$ and $(CH_2)_3NH_2^+$, the outcome is a series of perovskite compounds of $[AmineH^+][M(HCOO)_3^-]$,[63] with NaCl-type frameworks of $[M^{II}(HCOO)_3^-]$ of $4^{12}{\cdot}6^3$ topology (Fig. 13(b)). The linkages between metal sites are also 2.11-*anti-anti* formates and the cations are in the cubic cavities of the framework. We have recently found that guanidinium can also be incorporated in this type of metal–formate framework.[64] However, employment of bulky $AmineH^+$ cations such as $(CH_3CH_2)_3NH^+$$(CH_3CH_2)_2NH_2^+$ and $CH_3CH_2CH_2NH_3^+$ resulted in the porous $[M_3(HCOO)_6]$ family (discussed below). Very recently, this study has been expanded into investigating diamines and polyamines, and the outcomes appear to be very interesting. For example, the employment of protonated *N*,*N′*-dimethylethylenediamine ($dmenH_2^{2+}$) has templated the formation of a novel binodal metal–formate framework of $(4^{12}{\cdot}6^3)(4^9{\cdot}6^6)$ topology (Fig. 13(c)), closely related to minerals of niccolite (NiAs) and colquiriite ($LiCaAlF_6$).[65] These materials, in most cases, show 3D long-range antiferromagnetic ordering with weak ferromagnetism arising from the antisymmetric exchange *via* the formato bridges, and in some cases spin re-orientation occurs. The critical temperatures can be as high as 30 K (for Ni compounds). We believe that the metal–formate frameworks display significant malleability and adaptability to protonated amine templates, and we expect that new metal–formate compounds with novel structures and topologies, and interesting magnetic properties will likely result when different di- or polyammonium templates are employed.

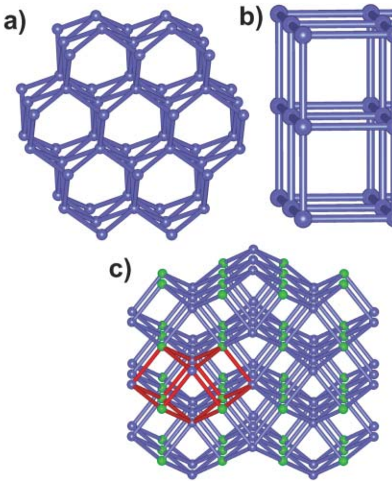


Fig. 13 Topological plots of the three-dimensional anionic metal–formate frameworks templated by (a) NH_4^+, (b) $CH_3NH_3^+$ and (c) $dmenH_2^{2+}$. Spheres are metal ions and sticks 2.11-*anti-anti* formato bridges. In (c) one cavity is highlighted in red, and green spheres are $(4^{12}{\cdot}6^3)$ node, blue spheres $(4^9{\cdot}6^6)$ node.

Finally, a novel family of porous magnets, $[M_3(HCOO)_6]$, where M = Mn, Fe, Co and Ni, have been recently discovered independently by several groups and by us,[66–70] and this family now includes diamagnetic metals such as Mg and Zn.[69,70] Although several groups synthesized the compounds through solvothermal routes,[67–69] we first demonstrated that the compounds could be easily prepared by a simple solution chemistry method at ambient temperature, in which bulky protonated amines such as triethylamine, diethylamine or propylamine were employed.[66,70] We believe that the bulky ammonium ions inhibit the formation of the aforementioned anionic frameworks, as what was observed for the amine cations of smaller size. The isostructural members of this family possess porous diamondoid frameworks consisting of the apex-sharing M-centered MM_4 tetrahedron nodes (Fig. 14(a) and (b)), in which all metal atoms are octahedral. The MM_4 tetrahedron node has one central M^{2+} ion, four apical M^{2+} ions, and six edges of $HCOO^-$ groups, which link the metal ions in 3.12-*syn-syn*/*anti* mode. The framework

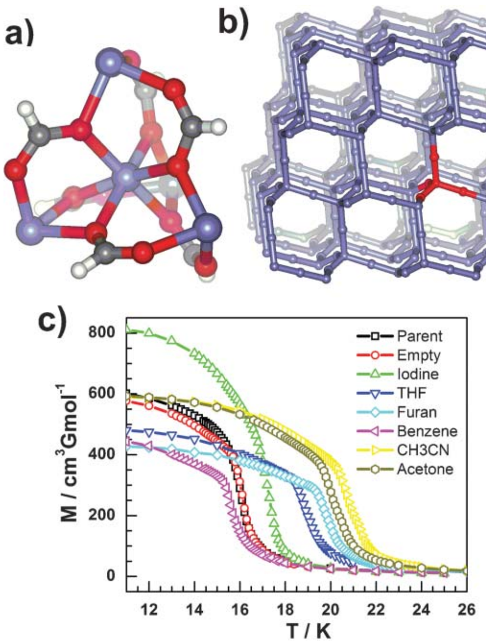


Fig. 14 The structure of the porous diamond framework of $[M_3(HCOO)_6]$ formed by the M-centred MM_4 tetrahedra as nodes sharing apices and showing open channels. (a) The MM_4 tetrahedron unit. Color scheme is M blue, C grey, H white, O red. (b) The diamond framework with one MM_4 tetrahedron highlighted in red. (c) FC measurements of $[Fe_3(HCOO)_6]$ and its guest-inclusion compound series with the guest names shown under an applied field of 10 Oe. Parent is the parent compound with guests of methanol and water and Empty is the framework without guest.

has high stability and flexibility to allow the easy removal of solvents and further inclusion of many types of guest, without damaging the crystallinity of the crystals. This provides the opportunity to study the guest-inclusion behavior by single crystal X-ray diffraction. The guest molecules usually form zigzag molecular arrays in the channels of host framework, and the host–guest H-bonding provides the primary host–guest interaction. In respect to magnetism, Mn and Fe members are considered as ferrimagnets with critical temperatures of 8.0 and 16.1 K, respectively, the Co analogue is probably an antiferromagnet with a spin canting below 2 K, and the Ni compound might show 3D long-range ferrimagnetic ordering at 2.7 K.[66,67] the Mn and Ni compounds are soft magnets while the Fe compound is quite a hard magnet. Guest-dependent magnetism has been observed and investigated for Mn and Fe frameworks. They display guest-modulated critical temperature. For the Mn frameworks, the T_C's were modulated by guests in the range of 4.8 to 9.7 K, compared with 8.0 K for $[Mn_3(HCOO)_6]$ without guest, while for Fe, the T_C changes from 15.6 to 20.7 K compared to 16.1 K for the guest-free $[Fe_3(HCOO)_6]$ (Fig. 14(c)), together with higher coercive fields (H_C) and remnant magnetizations (R_M) for the guest-inclusion materials with higher T_C. The guest-sensitive magnetism might arise from (a) the subtle changes in the important M–O–M angles of the host framework, where materials with larger M–O–M angles have lower T_C, and (b) host–guest interactions, mainly the H-bonds, where the existence of more strong host–guest H-bonds seems to favor higher T_C. Finally, a series of mixed-metal porous magnets of $[Fe_xZn_{3-x}(HCOO)_6]$ could be prepared due to the isomorphic nature of the $[M_3(HCOO)_6]$ family.[66d] The mixed-metal series exhibits systematic change from 3D long-range ordering to spin glass to superparamagnet and finally to paramagnet upon the increase of diamagnetic component of zinc in the series.

5 Conclusions

In this article, by our own work we have demonstrated that, the versatility of both coordination mode and magnetical transmission of several three-atom bridges allowed us to prepare various molecular magnetic systems, varying from SMMs, SCMs, to higher dimensional magnets, and even multifunctional materials such as photoactive and porous magnets. These effective magnetic couplers, whether having been widely employed (such as azido) or not (such as formato and hydrogencyanamide), still provide new opportunities to design and create novel molecular-based magnetic materials. The incorporation of various co-ligands and/or templates provides a route for systematic design and successful dimensionality modulation of these materials. Furthermore, these organic components in the inorganic–organic hybrid materials can be carefully tailored with specific functions and properties, which will result in multifunctionality. Other transition metal centers, such as the air-sensitive V^{2+} and Cr^{2+} and the 4d/5d transition metals, and other bridging co-ligands/templates with different connectivities and additional functions, such as chirality and photoreactivity, will be featured in future investigations.

Acknowledgements

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