2D warp-and-woof interwoven networks constructed by helical chains with different chirality†

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Two unprecedented 2D entangled layers of warp-and-woof threads interwoven by left- and right-handed helical chains, $\{[Mn(salen)Au(CN)_2]_4(H_2O)\}_n$ (salen = *N*,*N*′-ethylenebis(salicylideneaminato)) 1 and $\{Mn(acacen)Ag(CN)_2\}_n$ (acacen = *N*,*N*′-ethylenebis(acetylacetonylideneiminate)) 2, have been synthesized and characterized.

Currently, the rational design and synthesis of coordination polymer frameworks continue to attract considerable interest not only because of their potential applications in optical, magnetic and electronic materials, but also due to the intriguing variety of topologies and entanglement motifs.[1] Interwoven networks, an important array of entanglement, represent an opportunity for achieving a 1D to 2D dimensional expansion through interweaving of 1D chains. However, dimensional expansion based on only single chain structures is still very rare.[2] Also rare, on the other hand, is entanglement of 1D chains with unusual topologies.[3]

The linear dicyanoaurate anion $[Au(CN)_2]^-$, which can bridge coordination centers through two cyano groups and form weak intramolecular Au···Au interactions (aurophilic interactions),[4] is an ideal building block for preparing heterometallic coordination polymers.[5,6] Aurophilic interactions have a similar strength to hydrogen bonding.[4,7] Besides the metal–ligand coordinate bond framework, structural dimensionality can be increased effectively through such weak aurophilic interactions.[9e] The d^{10} metal anion, $[Ag(CN)_2]^-$, has a similar chemical structure to $[Au(CN)_2]^-$ and can also form Ag···Ag argentophilic interactions. Because of the weak metal–metal interactions, $[M(CN)_2]^-$ (M = Au and Ag) have been widely involved in interpenetrating structures and many fascinating networks with intriguing topologies have been explored.[5,8–10]

We report here two new 2D entangled arrays obtained from the reactions of $[M(CN)_2]^-$ (M = Au (**1**) and Ag (**2**)) and $[Mn^{III}(L)]^+$ (L = salen: *N*,*N*′-ethylenebis(salicylideneaminato) (**1**) and acacen: *N*,*N*′-ethylenebis(acetylacetonylideneiminate) (**2**)).‡ **1** and **2** possess the same novel 2D warp-and-woof layer structure weaved by helical chains with different chirality. The 1D left- and right-handed helical chains are interwoven nearly orthogonally to form a 2D clothlike network and the interwoven chains are cross-linked *via* aurophilic and argentophilic interactions (Fig. 1).

X-Ray crystallography§ reveals that there are four crystallographically independent Mn and four independent Au in the asymmetric unit of **1**. Each manganese ion is six-coordinated and displays a distorted octahedral geometry of MnN_4O_2 (Fig. S1, ESI†). Two nitrogen atoms and two oxygen atoms of the salen ligand define the equatorial plane around Mn(III) ion, Whereas the axial sites are occupied by two nitrogen atoms of $[Au(CN)_2]^-$. The nearly linear $[Au(CN)_2]^-$ groups link Mn^{III}(salen) moieties into infinite 1D chains containing [Mn–NC–Au–CN] repeating units. All the Au(I) ions are involved in aurophilic interactions with Au(I) ions in other chains vertical to it with distance Au(2)···Au(3) 3.0960(13) Å, significantly shorter than those reported in the literature.[5a,c,e,9d,f,11,12] which results in the formation of a 2D interwoven network. The water (O9) is linked by O–H···O to adjacent O6 and O8 with O···O distances of 2.876 and 2.873 Å.

Within the 2D network of **1**, all the 1D chains run in two nearly perpendicular directions and interweave in a ‘one-over/one-under’ fashion. The chains vertical to each other are cross-linked by aurophilic interactions, generating a 2D entangled woof and warp threaded layer with an uncommon topology (Fig. 1). This kind of clothlike structure is very rare in coordination polymers[13] and has not been discriminated by using the common topological indices.[3]

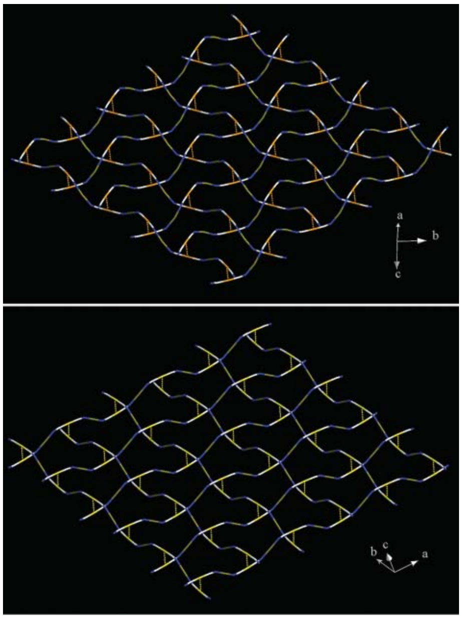

Fig. 1 Extended 2D interwoven network of **1** (top) and **2** (bottom). Au = light orange, Ag = light yellow, Mn = dark yellow, N = blue, C = white, Salen groups have been omitted for clarity.

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More interestingly, all the 1D chains in **1** are arranged into a helical mode. This is unprecedented in systems containing $[Au(CN)_2]^-$. In general, the formation of helices is a consequence of the characteristics intrinsic to helical components.[14] However, neither $[Au(CN)_2]^-$ nor $[Mn^{III}(salen)]^+$ have the intrinsic tendency to form helical structures, therefore the structure of **1** is intriguing. In fact, no helical complex based on $[Au(CN)_2]^-$ building blocks have been prepared previously and as far as we know, this is the first 2D interwoven network constructed by helical chains.

The most fascinating and unusual structural feature is that the interwoven helical chains in **1** have different chirality: one is left-handed while the other is right-handed (Fig. 2), though they have the same components and linking sequence. Helices with different chiralities coexisting in the same system are rare,[15] while 2D interwoven networks weaved by helices with different chirality is also unprecedented, which makes **1** a new interesting member of 2D interwoven networks.

The interwoven network of **1** is stabilized by two types of π–π interactions arising from the aromatic rings of the salen ligands in the adjacent layers. One is offset face-to-face stacking[16] with face-to-face and centroid-to-centroid distances of *ca.* 3.50 and 3.82 Å, the other is edge-to-face stacking with distance of 3.5039 Å (the angle of the two interacted phenyl planes is 81.4°). The 2D interwoven networks are stacked into 3D networks in a parallel manner with metal ions staggered to each other.

Compound **2** has a similar 2D interwoven layer structure to **1**. Unlike **1**, the asymmetric unit of **2** comprises two $[Mn(acacen)Ag(CN)_2]$ units, one in a general position (Mn1) and two crystallographically unique half-occupancy Mn(III) ions (Mn2 and Mn3) lying on the twofold axes. The weft chain contains only Mn1 and the warp contains Mn2 and Mn3 (Fig. S2, ESI†). All Mn(III) ions display a distorted octahedral geometry of MnN_4O_2. Mn(III)(acacen) moieties are linked by the linear $[Ag(CN)_2]^-$ groups into two kinds of infinite 1D helical chains, left- and right-handed. The helical chains with different chirality are almost vertical to each other and interweaved into a 2D entangled layer like woof and weft threads similar to **1** and are cross-linked by Ag···Ag interactions with Ag(1)···Ag(2) distance of 3.0965(9) Å, falling in the range of 2.9264–3.3897 Å reported in the literature.[17]

$[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$ have similar structures and chemical properties. But from the top view of the helical chains (Fig. 3), the holes of **1** are square and **2** are rectangular. The reasons for such a difference might be the coexistence of weak Au···Au interactions between two vertical interwoven chains and π–π interactions arising from the aromatic rings of salen ligands in adjacent layers in **1**, which pull the chains towards inside and outward directions. Since in **2**, only Ag···Ag interactions pull the chains towards inside directions, and with the absence of interactions outward, it only can form a rectangle helical hole. The Ag atoms are located on the short-edge and Mn(III) atoms reside in the long-edge of the rectangle. This also can be seen in the side view of the helices shown in Fig. 4.

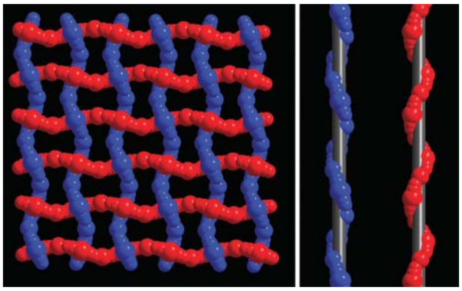

Fig. 2 Space-filling model of the 2D interwoven networks and left- and right-handed helical chains of **1**. (Blue: left-handed, red: right-handed; salen groups have been omitted for clarity.)

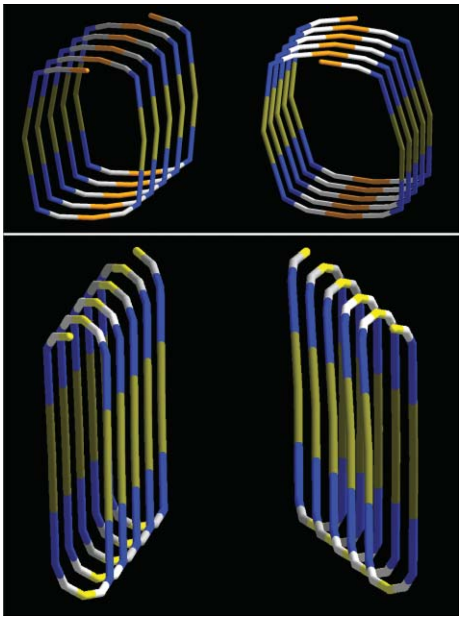

Fig. 3 Top view of left-handed and right-handed helical chains in **1** (top) and **2** (bottom).

The equivalent coexistence of left- and right-handed helices in **1** and **2** might due to that during the formation of helical chains, there exist an equilibrium between helices with different chirality, and no factor can provide a sufficient energy difference to move the equilibrium between left-handed and right-handed helices to one side only.[18]

The magnetic susceptibilities of **1** and **2** were measured from 2 to 300 K at an external magnetic field strength of 2000 Oe. The susceptibility data of **1** was fitted by a formula including both single ion zero-field splitting (*D*) and intermolecular effects with the use of molecular field approximation (*zJ*) and **2** was fitted by a one-dimensional chain formula. The best agreement between calculated and experimental values of the susceptibility was found

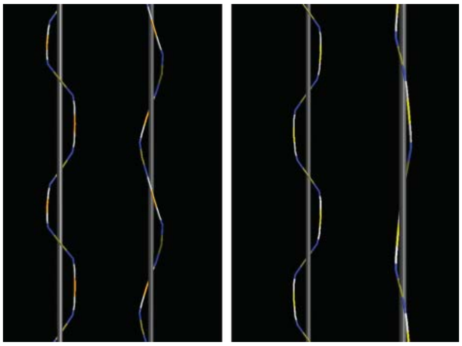

Fig. 4 Side view of left-handed helical chains in **1** (left) and **2** (right) along *a* and *c* axis.

with $zJ = 0.12$ cm^{-1}, $g = 2.02$, $D = -5.5$ cm^{-1}, $R = 6.4 \times 10^{-3}$ for **1** and $J = -0.1$ cm^{-1}, $g = 2.04$, $R = 5.3 \times 10^{-4}$ for **2**. These fits are indicated in Fig. 5 as solid lines.

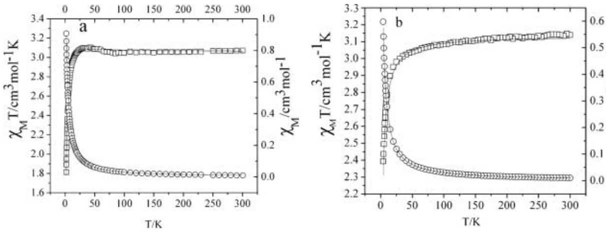

Fig. 5 Temperature dependence of $\chi_M T$ for **1** (a) and **2** (b) at a field strength of 2000 Oe.

In summary, two unprecedented 2-D interwoven networks constructed by left- and right-handed helical chains containing $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$ building blocks have been prepared and structurally characterized. The observed unusual features in their structure make **1** and **2** new intriguing members of 2D interwoven networks.

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Notes and references

‡ Complexes **1** and **2** were synthesized by the reaction of $[Mn(salen)(H_2O)_2]ClO_4$ (0.045 g, 0.1 mmol) and $K[Au(CN)_2]$ (0.03 g, 0.1 mmol) for **1** and Mn(acacen)Cl (0.032 g, 0.1 mmol) and $K[Ag(CN)_2]$ (0.02 g, 0.1 mmol) for **2** in MeOH–H_2O (25 mL, volume ratio 4 : 1) at room temperature. Brown block crystals were collected and air-dried after about two months. Yield: 0.03 g, *ca.* 60% for **1** and 0.02 g, *ca.* 50% for **2** based on Mn(III). IR (KBr): $\nu_{C\equiv N}$(cyanide) 2145 cm^{-1}, $\nu_{C=N}$(imine) 1625 cm^{-1} (**1**), $\nu_{C\equiv N}$(cyanide) 2148 cm^{-1}, $\nu_{C=N}$(imine) 1586 cm^{-1} (**2**).

§ *Crystal data*: $C_{72}H_{58}N_{16}O_9Au_4Mn_4$ **1**; $M = 2298.97$, triclinic, space group $P\bar{1}$, $a = 13.382(5)$, $b = 14.081(5)$, $c = 20.242(8)$ Å, $\alpha = 94.217(3)$, $\beta = 107.932(4)$, $\gamma = 90.853(6)°$, $V = 3616(2)$ Å^3, $Z = 2$, $D_c = 2.111$ g cm^{-3}, μ(Mo-Kα) = 8.824 mm^{-1}, $T = 293(2)$ K, $F(000) = 2180$. 28281 reflections collected, 17061 unique ($R_{int} = 0.0505$). The structure was solved by direct methods and refined on F^2 by the SHELX-97 program to $R1 = 0.0492$ ($wR2 = 0.1009$) with a goodness-of-fit of 0.965. CCDC 615649. $C_{28}H_{36}Ag_2Mn_2N_8O_4$ **2**; $M = 874.27$, monoclinic, space group $C2/c$, $a = 20.388(4)$, $b = 20.161(4)$, $c = 17.384(3)$ Å, $\beta = 105.690(3)°$, $V = 6880(2)$ Å^3, $Z = 8$, $D_c = 1.688$ g cm^{-3}, μ(Mo-Kα) = 1.883 mm^{-1}, $T = 294(2)$ K, $F(000) = 3488$. 17294 reflections collected, 6047 unique ($R_{int} = 0.0405$). The structure was solved by direct methods and refined on F^2 by the SHELX-97 program to $R1 = 0.0346$ ($wR2 = 0.0661$) with a goodness-of-fit of 1.029. CCDC 609524. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707356a

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