Unique 3D self-penetrating Co^{II} and Ni^{II} coordination frameworks with a new (4⁴.6¹⁰.8) network topology⁺

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Two unique six-connected self-penetrating coordination polymers with a new (4⁴.6¹⁰.8) network topology, derived from the cross-linking of two 6⁶-dia subnets, were constructed from Ni^{II} or Co^{II} and two types of V-shaped tectons. The Ni^{II} complex 1 shows an antiferromagnetic coupling *via* μ carboxylate and μ -H₂O pathways, whereas the Co^{II} complex 2 exhibits the single-ion behavior in 300–34 K and then a ferromagnetic coupling at lower temperatures.

Since the highly influential books of Wells,¹ the network topological approach, which is a powerful tool for constructing and analyzing network structures, has received an increasing level of attention.² To date, network topologies in coordination polymers have been discussed in several distinguished reviews,³ and abundant examples, from uninodal networks with 3–12 connectivity, to mix-connected networks including (3,4)-, (3,6)-, (4,6)- and (4,8)-connected types, have been reported.⁴ Undoubtedly, these significant results extend our understanding and open up new opportunities for further developing such net-based solid-state materials.

Meanwhile, particular attention has been devoted to entangled systems for their undisputed beauty and potential applications as molecular-based materials. As a result, a variety of novel entangled systems, such as interpenetrating, polycatenating, polythreading, and polyknotting, have been discovered thus far.⁵ Despite the meaningful progress in this hotspot, there is an unfavorable lack of systematic and characteristic researches on more sophisticated entangled architectures, especially cases for the relatively unusual self-penetrating (or polyknotting) structures. In contrast to interpenetrating networks, self-penetrating nets, as the extended equivalents of molecular knots, is still in its growing period.^{3c,6} On the other hand, nodes of 3-, 4-, and 6-connectivity are of

most relevance, and numerous such network topologies have been known.^{3,4} However, examples for 6-connected self-penetrating nets are quite rare,⁷ implying a challenging issue because it is difficult to predict such target materials prior to synthesis.

As present, a particularly promising approach for the creation of self-penetrating topologies is to use metal clusters with suitable geometry and connectivity as the net nodes in virtue of a rational design of organic ligands.8 In this respect, V-shaped building blocks can serve as excellent candidates to construct unusual entangled frameworks due to their specific backbones, often flexible.9 Very recently, by using the V-shaped polycarboxylate tectons, we have successfully obtained the first armed-polyrotaxane 1D array based on loop chains with side arms, and a unique 3D 8-connected self-penetrating coordination network based on hexanuclear Pb^{II} clusters.¹⁰ As an extension of our work, we combine two types of Vshaped building blocks, 4,4'-sulfonyldibenzoic acid (H₂sdba) and 4,4'-dipyridyl-sulfide (dps), into one assembled system to afford two coordination frameworks $\{[M(sdba)(dps)(H_2O)_{0.5}](H_2O)_{1.2}\}_n$ $(M = Ni^{II} \text{ for } 1 \text{ and } Co^{II} \text{ for } 2)$. Both complexes show the unique $3D(4^4.6^{10}.8)$ topological networks with a self-penetrating feature, which consists of the "warp and weft" interwoven fabric motifs of the helical subunits.

Complexes 1 and 2 were prepared by hydrothermal reaction of Ni^{II} or Co^{II} acetate, H₂sdba, dps, and NaOH,¹¹ which were characterized by IR spectra, elemental analysis, PXRD, and TGA techniques (see Fig. S1, ESI†).

Single-crystal X-ray analysis¹² indicates that 1 and 2 are isomorphous. Therefore, only the structure of 1 will be discussed as a representative. The asymmetric unit of 1 contains one Ni^{II} center, one sdba anion, one dps linker, half aqua ligand, and lattice water molecules. Among them, the half aqua ligand has its oxygen atom on a crystallographic two-fold axis, there are two lattice water molecules which lie at special positions in the Fddd space group, but for O2W water oxygen atom, its anisotropic displacement parameters is very large. In order to give a better reasonable model, we have tried many times and then gave a final occupancy of only 0.1 for it in the asymmetric unit, even though it is at a site involved with three two-fold axes. Water O1W lies on a two-fold axis and its occupancy was normal 0.5. As shown in Fig. 1(a), each Ni^{II} ion takes a distorted octahedral geometry, which is provided by three carboxylate oxygen atoms of two sdba2- ligands, two pyridyl nitrogen donors of a pair of dps, and one aqua molecule. In this structure, each dps and aqua play the bridging role to link the Ni^{II} centers, and as for sdba²⁻, its two carboxylate groups display the monodentate and μ -O,O' coordination modes, respectively, featuring a μ_3 -linker. In this way, two adjacent Ni^{II} centers are connected by a pair of carboxylate groups and one water bridge to form a dimeric unit (the adjacent Ni \cdots Ni distance = 3.510 Å), and

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Fig. 1 (a) Coordination environment of Ni^{II} (symmetry codes: A = -x - 1/2, -y + 1/2, -z + 1; B = x + 1/4, -y + 1/2, z - 1/4; C = -x, y - 1/4, z - 1/4). (b) Self-penetrating 6-connected network with (4⁴.6¹⁰.8) topology. (c) Two parallel **dia** subnets. (d) Schematic view of the self-penetrating structure.

such dimeric secondary building units (SBUs) are further extended by the sdba²⁻ ligands to afford a very complicated 3D network (see Fig. S2, ESI†). In addition, strong O–H···O H-bonds between water ligands (O7) and uncoordinated carboxylate groups (O2) (O···O: 2.574, 159.34°) also stabilize the whole structure.

In order to clearly understand such a 3D architecture, the topological method is used to simplify the structure. Topologically, by regarding each Ni₂-SBU as a network node, the overall 3D net can be rationalized as a uninodal 6-connected framework with the point symbol of $(4^4.6^{10}.8)$ (Fig. 1(b), vertex symbol: [4.4.4.4.6_3.6_3.6_5.6_5.6_5.6_6.6_6.6_6.6_8_9], named as **net B**). Further analysis of this structure indicates that it consists of two interpenetrating 4-connected diamonds (**dia**) of Class IIa (related by an inversion center) nets with dimeric Ni^{II} nodes (see Fig. 1(c)) and sdba²⁻ connectors, which are interconnected by the dps pillars. Within this network, the 6-membered circuits mutually interweave into a novel self-penetrating motif (see Fig. 1(d)).

Notably, 6-connected self-penetrating networks are quite rare, and there is an interesting relationship between the current **net B** and other reported 6-connected self-penetrating types: (4⁴.6¹⁰.8) (mab),^{7a-d} (4⁴.6¹⁰.8) (roa),^{7b,e,f} (4⁸.6⁶.8) (rob),^{7b,g} (4⁴.6¹¹),^{7h} and (4⁸.6⁷).⁷¹ Following the topological approach proposed for the analysis of high connectivity materials,^{3b} all above-mentioned 6-connected nets are based on square layers (4^4 -sql). Notably, the most difference between our net B and other 6-connected self-penetrating nets is the presence of unusual parallel interpenetration of two identical dia subnets, and an analysis of the interpenetrating topology with the TOPOS program¹³ suggests that it belongs to class IIa, that is, the individual nets are related by means of a full interpenetration symmetry element. In addition, net B is closely related to, but different from those of mab and roa. In the latter three cases, the similar 6-connected self-penetrating nets have the same Schläfli symbol (4⁴.6¹⁰.8), but with different vertex symbols for **mab** of $4.4.4.4.6_4.6_5.6_5.6_5.6_5.6_{11}.6_{11}.6_{11}.6_{11}.*$ net B can be classified as the first six-connected self-penetrating network based on **dia** subnets interpenetrated by non-translational symmetry operation (Class IIa).

As expected, with topological analysis guidance, the complicated structure of 1 can be clearly understood as a combination of dia subnets and pillars. Each dimeric Ni^{II} SBU acts as a tetrahedral node via the linkage of V-shaped sdba2- connecters to form a typical dia network. The large diamondoid cages in each net have the maximum dimensions of $42.96 \times 40.06 \times 33.86$ Å (see Fig. S3(a), ESI[†]), which allows the other selfsame dia network to penetrate and thus, forms a 2-fold interpenetrating array (see Fig. 2(a)). Despite interpenetration, the framework of 1 remains open, and contains 1D channels of approximate 13.59 \times 8.42 Å along [100], in which the lattice water molecules are located. The potential solvent-accessible areas before and after the exclusion of the water guests are as large as 7025.6 and 7409.3 $Å^3$ (35.7% and 37.7% of the unit cell volume), as calculated by the PLATON software.14 Another fascinating structural feature of 1 is to form a novel "warp and weft" like interwoven fabric structure (see Fig. 2(b)). As illustrated in Fig. 2(c), the dimeric Ni^{II} SBUs are bridged by the sdba²⁻ spacers into pairs of heterochiral helical chains, with the pitch of 20.828 Å. Interestingly, pairs of homochiral side-by-side double helix from two individual dia nets are laid one over the other alternately, which leads to the "warp and weft" type 2D nets along the ab plane (see Fig. 2(b)). In this condition, two dia networks are composed of pairs of such "warp and weft" type 2D networks in an alternate fashion (see Fig. S3(b), ESI[†]). Although several "warp and weft" type coordination polymers based on 1D tectons have been reported.¹⁵ such helical interwoven fabric structural motif in 1 is unique. Further, the Vshaped dps ligands serve as pillars to join the neighboring dimeric Ni^{II} SBUs to 1D quadrate loops (see Fig. S3(c), ESI[†]), which interlink the two dia networks to produce the final self-penetrating pattern (see Fig. 1(d) and 2(d), Fig. S3(d), ESI[†]).



Fig. 2 (a) Two fold interpenetrating **dia** network. (b) The "warp and weft" interwoven fabric structure along the *ab* plane constructed by pairs of homochiral (blue/yellow for left- or teal/purple for right-hand) side-by-side double helix from two individual **dia** nets. (c) The **dia** subnet constructed by heterochiral helical chains. (d) 3D coordination network with 1D quadrate loops and **dia** subnets.

TGA curves of complexes **1** and **2** are similar, probably because of their isostructural nature (see Fig. S4, ESI[†]). Complex **1** is used

as an example. The first weight loss of 3.8% corresponds to the removal of 2.25 water molecules per formula unit (calc. 3.35%). From *ca*. 250 °C the expulsion of organic components occurs. The final residue seems to be NiO (observed: 13.9% and calculated: 13.07%), which has also been further confirmed by temperature-variable PXRD patterns of **1** (see Fig. S1(b), ESI†).

The magnetic susceptibilities (χ_M) of **1** and **2** were measured in 2–300 K (see Fig. 3). For **1**, the $\chi_M T$ value at room temperature is 1.55 cm³ K mol⁻¹, which falls in the normal range of two noncoupled Ni^{II} ions. As the temperature is lowered, the $\chi_M T$ decreases slowly until *ca*. 50 K, and then sharply to 0.53 cm³ K mol⁻¹ upon cooling to 2 K, indicating a dominant antiferromagnetic coupling. In order to quantitatively evaluate the magnetic interactions, the following equation for a dinuclear Ni^{II} model is derived from the Hamiltonian $\hat{H} = JS_1S_2$,¹⁶ where J is the intradimer exchange constant. A least-squares fit of the magnetic susceptibilities data led to J = -1.15 cm⁻¹, g = 2.49, and $R = 3.02 \times 10^{-4}$. The negative J value indicates a weak antiferromagnetic interaction between the adjacent Ni^{II} ions.

$$\chi_{M} = \frac{Ng^{2}\beta^{2}}{KT}\frac{A}{B}$$
$$A = 2\exp\left[\frac{J}{KT}\right] + 10\exp\left[\frac{3J}{KT}\right]$$
$$B = 1 + 3\exp\left[\frac{J}{KT}\right] + 5\exp\left[\frac{3J}{KT}\right]$$



Fig. 3 Temperature dependence of $\chi_M T$ and χ_M for **1** (a) and **2** (b). Open points are the experimental data, and the solid line represents the best fit obtained from the Hamiltonian given in the text.

For 2, spin-orbital coupling of the Co^{II} ion gives rise to a $\chi_{\rm M}T$ value of 4.5 cm³ K mol⁻¹ at room temperature, which is much higher than that of two non-interacting Co^{II} ions (3.75 cm³ K mol⁻¹ assuming g = 2.0). The $\chi_M T$ decreases as cooling and has a minimum of 3.15 cm³ K mol⁻¹ (see Fig. 3(b)). In the region of 300-34 K, complex 2 mainly shows the single-ion behavior of Co^{II}. Below 34 K, a ferromagnetic coupling between Co^{II} overcomes the effect of spin-orbital coupling and thus, compensates the decrease of $\chi_{\rm M} T$, leading a sharp increase of $\chi_{\rm M} T$ to a maximal value of 4.6 cm³ K mol⁻¹ at 14.9 K, which however, cannot give a ground state spin of $S_{\rm T} = 3$. Temperature dependence of the reciprocal susceptibility $(\chi_{\rm M}^{-1})$ above 50 K follows the Curie–Weiss law $(\chi_{\rm M} =$ $C/(T-\theta)$) with a Weiss constant $\theta = -4.65$ K and a Curie constant $C = 4.40 \text{ cm}^3 \text{ K mol}^{-1}$. This contribution of spin-orbital interaction diminishes the ferromagnetic exchange, resulting in a negative Weiss constant.

$$\begin{split} \hat{H} &= -2J\hat{S}_{1}\hat{S}_{2} = -J(\hat{S}_{T}^{2} - \sum_{i=1}^{2}\hat{S}^{2}) \\ \chi_{M} &= \frac{Ng^{2}\beta^{2}}{3kT} \times \frac{84e^{12J/kT} + 30e^{6J/kT} + 6e^{2J/kT}}{7e^{12J/kT} + 5e^{6J/kT} + 3e^{2J/kT} + 1} \\ &= \frac{2Ng^{2}\beta^{2}}{kT} \times \frac{14e^{12J/kT} + 5e^{6J/kT} + e^{2J/kT}}{7e^{12J/kT} + 5e^{6J/kT} + 3e^{2J/kT} + 1} \end{split}$$

In summary, we have prepared two unique six-connected selfpenetrating 3D coordination frameworks, which can interestingly be regarded as the cross-linking of two interpenetrating **dia** subnets. This unique structural example will enrich our knowledge of network topologies and suggest the great potential of constructing unusual entangled networks from the V-shaped tectons, which are under way in our lab.

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- 11 Preparation of **1**. A mixture of Ni(OAc)₂·4H₂O (24.9 mg, 0.1 mmol), H₂sdba (30.6 mg, 0.1 mmol), dps (18.8 mg, 0.1 mmol) and NaOH (8 mg, 0.2 mmol) in H₂O (10 mL) was placed in a Parr Teflon-lined stainless steel (25 mL) autoclave, and heated to 160 °C for 5 days. Green block crystals of **1** were obtained in 58% yield (based on Ni^{II}). Anal. calcd for C₄₈H₃₆₄N₄O₁₄₂S₄Ni₂: C, 50.48; H, 3.21; N, 4.91%. Found: C, 50.23; H, 3.23; N,4.87%. IR (KBr, cm⁻¹): 3435 m, 2995 s, 1593 s, 1552 s, 1432 s, 1386 m, 1299 m, 1216 m, 1141 m, 1066 s, 922 w, 819 s, 761 w, 733 m, 630 s, 472 w. Preparation of **2**. An identical procedure to that of **1** was used except Ni(OAc)₂·4H₂O was replaced by Co(OAc)₂·4H₂O (24.9 mg, 0.1 mmol). Pink block crystals of **2** were obtained in 50% yield (based on Co^{II}). Anal. calcd for C₄₈H₃₆₄N₄O₁₄₂S₄Co₂: C, 50.46; H, 3.21; N, 4.91%. Found: C, 50.20; H, 3.21; N, 4.86%. IR (KBr, cm⁻¹): 3438 m, 2987 s, 1588 s, 1559 s, 1436 s, 1380 m, 1291 m, 1221 m, 1148 m, 1069 s, 918 w, 822 s, 766 w, 738 m, 638 s, 477 w.
- 12 Crystallographic data for **1** (CCDC: 778541): $C_{48}H_{36,4}N_4O_{14,2}S_4N_{12}$, Mr = 1142.07, orthorhombic, Fddd, a = 11.466(1), b = 39.891(3), c = 43.067(4) Å, V = 19699(3) Å³, Z = 16, $\rho_c = 1.54$ g cm⁻³, $\mu = 1.006$ mm⁻¹, S = 0.81, $R_{int} = 0.0373$ (for 4575 unique reflections), $R_1 = 0.0708$ and $wR_2 = 0.1730$. Crystallographic data for **2** (CCDC: 778542): $C_{48}H_{36,4}N_4O_{14,2}S_4Co_2$, Mr = 1142.55, orthorhombic, Fddd, a = 11.418(1), b = 40.061(4), c = 42.963(4) Å, V = 19653(3) Å³, Z = 16, $\rho_c = 1.544$ g cm⁻³, $\mu = 0.917$ mm⁻¹, S = 1.053, $R_{int} = 0.0718$ (for 4574 unique reflections), $R_1 = 0.0412$ and $wR_2 = 0.0865$.
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