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Molecular Fabric Structure Formed by the 1D Coordination Polymer, $[Pb(bpe)(O_2CCH_3)(O_2CCF_3)]$

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ABSTRACT: Crystallization of *trans*-1,2-bis(4-pyridyl)ethylene (bpe) with Pb^{II} acetate in the presence of CF_3COOH yielded $[Pb(bpe)(O_2CCH_3)(O_2CCF_3)]_n$, and the solid-state structure contains spiral 1D coordination polymers entangled in a "warp and weft" interwoven structure. The absence of any weak interactions between the tangled strands in the 2D sheets make this a true molecular fabric structure.

Considerable progress has been made on the design and construction of multidimensional metal organic frameworks in recent years, owing to their intriguing structural topologies and potential application as functional materials.[1,2] The interwoven[3–6] structures assembled from 1D coordination polymers show quiet interesting structural features and are attractive because of their fascinating properties.[4] Many of these 1D coordination polymeric structures can be classified as normal 2D sheets because it is not possible, in principle, to remove individual strands without breaking the bonds within the networks, and hence, they have been separately studied as entangled structures.[2,7] In 2D metal organic frameworks, honeycomb, grid, brick-wall, square-grid, herringbone, long- and short-brick, and basket-weave networks are already known but the interwoven fabric structures are rare.[2] Hence, construction of such entangled networks from single-coordination polymer chains is still a challenge in crystal engineering. Although a few interwoven structures have been reported in the literature, only two structures are known as "warp and woof" like sheets formed from 1D zigzag coordination polymer strands.[5a,6] Ciani and co-workers have described "warp and woof" sheets, which represent the first "one-over/one-under" (1O/1U) interwoven network of 1D coordination polymer strands.[5b] A Hg^{II}-containing 1D coordination polymer reported the first "two-over/two-under" (2O/2U) 2D weave structure formed from 1D zigzag polymer chains passing through perpendicular fashion.[6] Recently, Moutos and co-workers have designed 3D interwoven fibers of biocompatible material that show good mechanical properties and provide an exciting opportunity for cartilage tissue engineers.[8] These fibers were developed by a microscale three-dimensional weaving technique to produce scaffold from yarn. This literature has revived our interest in fabric-like interwoven coordination polymers. Here, we report a serendipitous synthesis of a "warp and weft" like interwoven fabric structure formed by spiral 1D coordination polymeric chains of the Pb^{II} complex.

A DMF solution of *trans*-1,2-bis(4-pyridyl)ethylene (bpe) was added to a mixture containing $Pb(O_2CCH_3)_2$ and trifluoroacetic acid. Colorless rod-like crystals of $[Pb(bpe)(O_2CCH_3)(O_2CCF_3)]_n$ (**1**) were formed after slow evaporation of a clear DMF solution.[9] The single-crystal X-ray diffraction studies[10] reveal that the asymmetric unit contains the basic building block of **1**, as shown in Figure 1. The highly distorted Pb^{II} metal center is strongly coordinated to the N atoms of two bpe ligands [Pb1–N1, 2.648(7) Å and Pb1–N2, 2.458(6) Å] and chelates to an actetate anion [Pb1–O1, 2.704(6) Å and Pb1–O2, 2.367(6) Å] and an oxygen atom of the $CF_3CO_2^-$ ligand [Pb1–O3, 2.583(6) Å]. The crystallographic inversion center and glide plane present at the centers of the carbon–carbon double bonds of the bpe ligand generate spiral 1D coordination polymers,

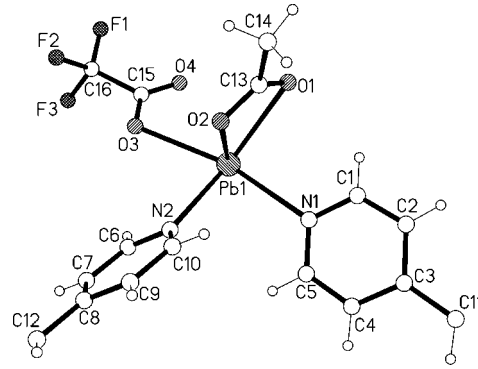

Figure 1. Diagram showing the asymmetric unit of **1**. Disordered F atoms are not shown. Bond distances (Å) and angles (deg): Pb(1)–O(2), 2.367(6); Pb(1)–N(2), 2.458(6); Pb(1)–O(3), 2.583(6); Pb(1)–N(1), 2.648(7); Pb(1)–O(1), 2.704(6); O(2)–Pb(1)–N(2), 78.0(2); O(2)–Pb(1)–O(3), 81.2(2); N(2)–Pb(1)–O(3), 75.8(2); O(2)–Pb(1)–N(1), 83.6(2); N(2)–Pb(1)–N(1), 83.4(2); O(3)–Pb(1)–N(1), 156.4(2); O(2)–Pb(1)–O(1), 50.80(18); N(2)–Pb(1)–O(1), 127.09(19); O(3)–Pb(1)–O(1), 104.6(2); N(1)–Pb(1)–O(1), 79.1(2).

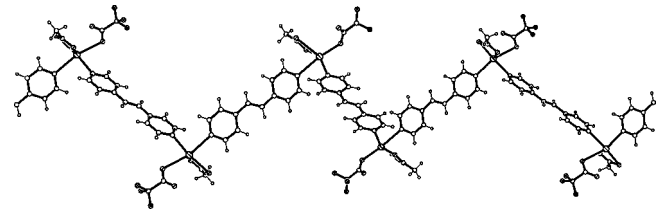

Figure 2. Perspective view of the 1D coordination polymeric strands formed by **1**. Disordered F atoms are not shown.

as shown in Figure 2. All of the strands are laid approximately along the *b* axis.

The spiral chains are running approximately in parallel but crossing over the C═C bond in perpendicular directions, as shown in Figure 3a. In **1**, each $[Pb(bpe)]_n^{2n+}$ strand crosses one over the next in almost parallel ABAB sequence, as shown in Scheme 1. The center of the double bonds in the bpe ligand containing the N2 atom is at the center of inversion, and hence, these bpe ligands in the crystal are interlaced. On the other hand, the other bpe ligands are aligned parallel when viewed from the *b* axis, as shown in Figure 3a. The bond angle between the metal and long-spacer ligands, i.e., N1–Pb1–N2 angle, 83.4(2)°, contributes to the formation of interwoven structures, as shown in Figure 3b.

The interwoven structure in the Au^I complex, $[(AuI_2)_2(mu\text{-}bis(diphenylphoshino)hexane)]_n$, contains interweaved 1D zigzag

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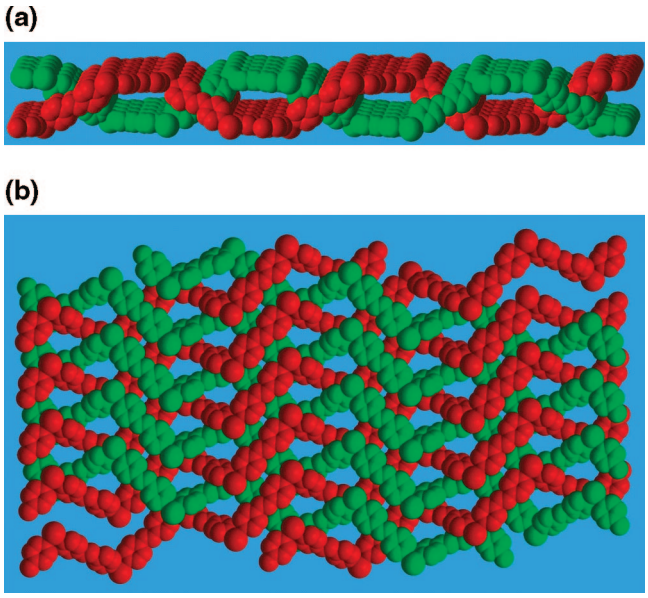
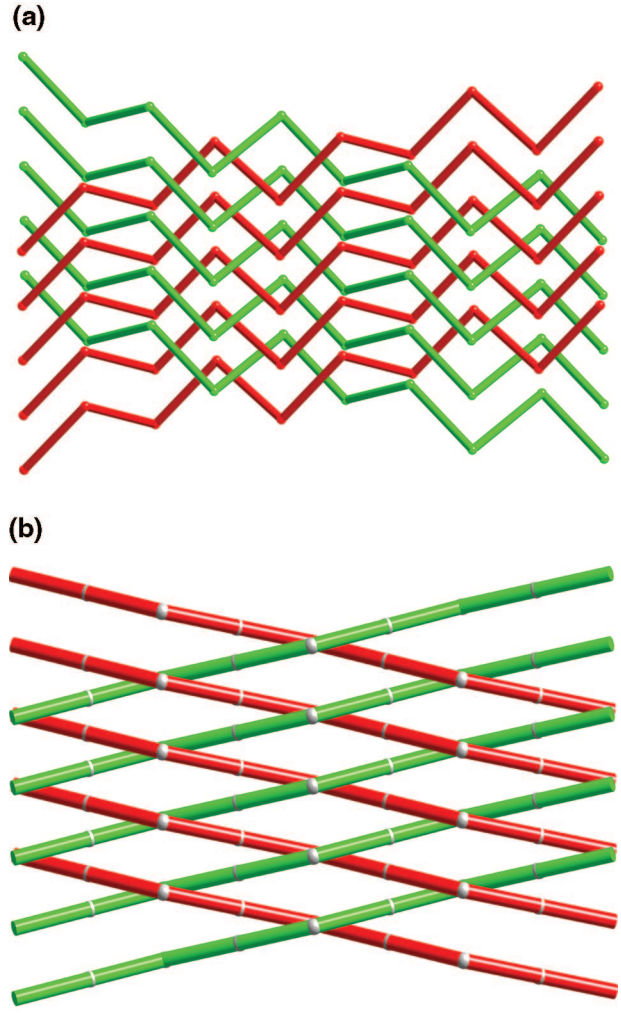


Figure 3. Space-filling models showing the interlacing, looking down from (a) the *c* axis and (b) the *a* axis.

Scheme 1. (a) Schematic diagram showing the details of interweaving by the spiral coordination polymeric strands in 1. The bend in the strands is due to the acute N–Pb–N angle. (b) Spiral coordination strands are straightened in this diagram to show the simplified interweaving pattern.



polymeric chains that are linked together through weak Au···Au interactions.[5b] A similar "warp and weft" complex {[Ag(L_2)(mu-PO_2F_2)$_{0.5}$](PF_6)$_{0.5}$}$_n$, (L_2 = 1-(isocyanidomethyl)-1*H*-benzo-trazole), also shows Ag–OPO–Ag bridges.[5e] These complexes form 2D sheets with a 1O/1U weaving pattern. The crystal structure [Cu(2,2′-bipy)(azpy)(H_2O)](NO_3)$_2$·H_2O is a unique example exhibiting "warp and weft" type supramolecular networks formed through interdigitated layers involving the $\pi\cdots\pi$ interaction of the 2,2′-bipy ligands.[5a] Another complex [$HgI_2(L_3)$], (L_3 = 2,6-bis(4-pyridinylmethyl)-benzo[1,2-*c*:4,5-*c*′]dipyrole-1,3,5,7(2*H*,26)-tetrone), represents the first 2O/2U 2D interwoven network formed through 1D coordination polymer chains in perpendicular orientation.[6] The formation of this 2D interwoven network has been interpreted by the contribution of a small N–Hg–N angle and short pyridyl arms.

The formation of the fabric structure via the C–H$\cdots\pi$ interaction of pyridyl rings in 4,4′-bipyridylethane was observed recently.[13] An unprecedented 3D interwoven network [Zn(phen)(L)]$_n$ (phen = 1,10-phenathroline, H_2L = *trans*-stilbene-4,4′-dicarboxylic acid) was formed with the assistance of the $\pi\cdots\pi$ interaction of zigzag polymer chains in four different directions.[3b] This structure shows "warp and weft" like 2D sheets with high porosity and guest selectivity. From all of these structures reported in the literature, it is clear that the presence of directional weak interactions is essential between the polymeric strands to form the "warp and weft" cloth structure. In **1**, all of the polymeric strands are laid one over the other alternately, which leads to ABAB-type entanglement in the *bc* plane, as shown in Figure 3b. The shortest distance between the centers of the adjacent interlaced C═C bond is 5.62 Å. Otherwise, there is no observable weak interactions between the interlaced coordination polymeric strands. Hence, this may be considered as the first true molecular fabric structure without any weak interactions between the strands in the interwoven structure. However, there exists a weak interaction between Pb^{II} and oxygen of the neighboring monodentate $CF_3CO_2^-$ anion (Pb1–O4, 2.835 Å), which makes this fabric structure form a 3D structure.

In summary, we have synthesized and characterized a novel 1O/1U "warp and weft" like interwoven fabric structure by the self-assembly of the bpe ligand with Pb^{II} ions. This provides an interesting supramolecular entanglement of a 1D polymer structure in the structural diversity of coordination polymers.

Acknowledgment. This research is supported by the National University of Singapore (Grant R-143-000-252-112).

Supporting Information Available: Crystallographic information in CIF format for compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Synthesis of a 0.5 mL DMF solution of *trans*-1,2-bis(4-pyridyl)ethylene (bpe, 91 mg, 0.5mmol) was mixed with a mixture of $Pb(OAc)_2 \cdot 3H_2O$ (189 mg, 0.5 mmol) and triflouroacetic acid (28 mg, 0.25 mmol) in 1 mL *N*,*N*-dimethylformamide (DMF). Slow evaporation of the clear solution formed colorless rod-like crystals after 2 days, decanted and dried under vacuo. Yield: 0.31 g (55%). IR (KBr, cm^{-1}) ν: 3446(w), 3048 (w), 2815(w), 2468(w), 2367(w), 1950(w), 1858(w), 1795(w), 1683(s), 1598(s), 1554(m), 1423(s), 1349(m), 1202(s), 1134(s), 1069(m), 999(m), 972(m), 832(s), 721(s), 664(m), 545(m). Elemental analysis (%) calcd for $C_{16}H_{13}N_2F_3O_4Pb_1$ (561.48): C, 34.23; H, 2.33; N, 4.99. Found: C, 34.05; H, 2.25; N, 4.86.

(10) X-ray crystallography: Intensity data for **1** were collected on a Bruker APEX diffractometer attached with a charge-coupled device (CCD) detector and graphite-monochromated Mo Kα radiation using a sealed tube (2.4 kW) at 223(2) K. Absorption corrections were made with SADABS,[11] and the crystallographic package SHELXTL[12] was used for all calculations. Cell Data: Orthorhombic space group *Ccca*, a = 20.347(1) Å, b = 39.859(2) Å, c = 9.3583(5) Å, V = 7589.8(7) Å^3, Z = 16, D_{calc} = 1.965 mg m^{-3}, μ = 8.942 mm^{-1}. Final R indices [$I > 2\sigma(I)$], R_1 = 0.0375, wR_2 = 0.1061, GooF = 1.050 for 2751 reflections and 246 parameters and R indices (all data), R_1 = 0.048, wR_2 = 0.112, GooF on F^2 = 1.053. Two sets of disordered F atoms were modeled (80/20) in **1**, which was deposited in the Cambridge Crystallographic Data Center (CCDC). See http://dx.doi.org.libproxy1.nus.edu.sg/10.1039/b123456 for crystallographic data in CIF format or other electronic formats.

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