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Communication

Pseudo-Polyrotaxane and β-Sheet Layer-Based Three-Dimensional Coordination Polymers Constructed with Silver Salts and Flexible Pyridyl-Type Ligands

Ming-Liang Tong,*,† Yin-Miao Wu,† Jie Ru,† Xiao-Ming Chen,*,† Ho-Chol Chang,‡ and Susumu Kitagawa*,‡

State Key Laboratory of Optoelectronic Materials & Technologies and School of Chemistry & Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China, and Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

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A fascinating 3D pseudo-polyrotaxane architecture with 1D polymeric $[Ag(bpp)]_n$ chains penetrating 2D (6,3) $[Ag_2(bpp)_2(ox)]_n$ sheets and a 3D coordination network constructed with 2D infinite $[Ag(ppa)]_n$ β-sheetlike layers pillared by ox ligands (bpp = 1,3-bis(4-pyridyl)propane; ppa = *N*-(4-pyridinylmethyl)-4-pyridinecarboxamide; ox = oxalate) have been prepared by utilizing flexible pyridyl-type ligands and have been crystallographically characterized. Crystal data for **1**: monoclinic, space group *C*2/*c*, $a = 7.619(2)$ Å, $b = 19.781(4)$ Å, $c = 26.799(5)$ Å, $\beta = 94.720(10)°$, $U = 4025.2(15)$ Å^3, and $Z = 4$. Crystal data for **2**: monoclinic, space group *C*2/*c*, $a = 28.947(8)$ Å, $b = 8.617(3)$ Å, $c = 16.307(6)$ Å, $\beta = 121.07(1)°$, $U = 3484(2)$ Å^3, and $Z = 4$.

Metal–organic coordination polymers have recently attracted great interest because of their potential applications in smart optoelectronic, magnetic, microporous, and biomimetic materials as well as their versatile intriguing architectures and topologies.[1,2] The design of coordination polymers is highly influenced by factors such as the coordination nature of the metal ion, the structural characteristics of the polydentate organic ligand, the metal–ligand ratio, and the possible counterion influence. In some cases, a subtle alteration in any of these factors can lead to new extended network structures. As a good candidate for rigid rodlike spacers in the construction of metal–organic polymers, 4,4′-bipyridine has been relatively well-known and has shown hundreds of interesting supramolecular architectures.[1] However, 1,3-bis(4-pyridyl)propane (bpp) and its analogues as the pyridyl-donor ligands similar to 4,4′-bipyridine have not been well explored to date, though several references have been documented.[3] We are trying to utilize flexible pyridyl-type ligands such as bpp and *N*-(4-pyridinylmethyl)-4-pyridinecarboxamide (ppa) to generate some novel polymers. In this Communication, we report the preparation and crystal structures of two novel 3D coordination networks self-assembled by $AgNO_3$, oxalate, and bpp or ppa ligands, namely $[Ag(bpp)][Ag_2(bpp)_2(ox)]NO_3$ (**1**) and $[Ag_2(ppa)_2(ox)]\cdot 9H_2O$ (**2**) (ox = oxalate), in which **1** is a rare 3D pseudo-polyrotaxane generated by the interpenetration of 1D polymeric $[Ag(bpp)]_n$ chains and 2D (6,3) $[Ag_2(bpp)_2(ox)]_n$ sheets (see later) and **2** is the first 3D coordination open network constructed by 2D infinite $[Ag(ppa)]_n$ layers pillared by ox ligands as connectors.

Both **1** and **2** were self-assembled by the silver(I) salts with bpp or ppa. An aqueous solution (5 cm^3) of $Na_2(ox)$ (0.5 mmol) and bpp or ppa (1.0 mmol) was added dropwise to a stirred MeCN solution (5 cm^3) of $AgNO_3$ (1.0 mmol) at 50 °C for 15 min. The resulting colorless solution was filtered and allowed to stand in air at room temperature for two weeks, yielding colorless crystals (ca. 45% and 70% yield

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* To whom correspondence should be addressed. E-mail: cestml@zsu.edu.cn (M.-L.T.); cescxm@zsu.edu.cn (X.-M.C.); kitagawa@sbchem.kyoto-u.ac.jp (S.K.).

† Sun Yat-Sen University.

‡ Kyoto University.

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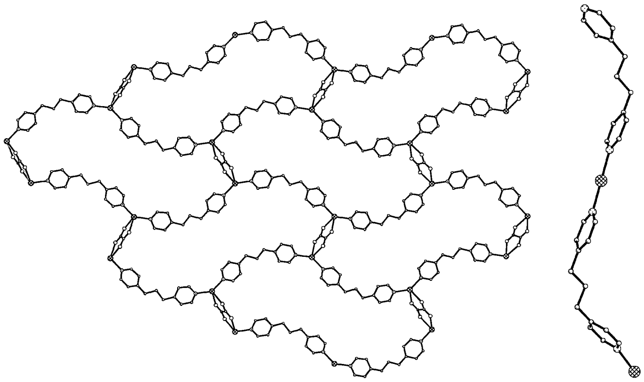

Figure 1. Left: 2D layer and hexagonal unit in **1**. Right: 1D polymeric chain in **1**.

for **1** and **2**, respectively). The elemental analysis and powder X-ray analysis confirmed the formulas of **1** and **2**.[4] It is noteworthy that different products isolated in the same reaction conditions may be attributed to the fact that bpp and ppa contain flexible hydrophobic and hydrophilic spacer linkers, respectively.

X-ray crystallography[5] has established that **1** is made up of 2D infinite neutral layers of (6,3) topology, 1D cationic chains, and nitrate counterions. As illustrated in Figure 1, each layer consists of $\mathrm{Ag^I}$ atoms connected by μ-bpp bridges and bis-chelated $\mathrm{ox^{2-}}$ bridges (in the ratio 2:2:1) and can be described in terms of identical (6,3) sheets with hexagonal $\mathrm{Ag_6(bpp)_4(ox)_2}$ units. Each $\mathrm{Ag^I}$ atom in the hexagonal unit is coordinated in a greatly distorted tetrahedral geometry with the two nitrogen atoms from different bpp ligands and the two oxygen atoms from a chelated ox ligand [Ag−N 2.226(3) Å; Ag−O 2.419(3) and 2.463(3) Å; N(O)−Ag−N(O) 67.59(9)−142.10(12)°]. All the $\mathrm{Ag^I}$ atoms and bpp and ox ligands in a layer are almost coplanar; adjacent sheets are stacked in an offset fashion along the *a*-axis so that the original large hexagonal motifs within each layer are therefore divided into two identical halves. The Ag(2) atoms in each polymeric chain are coordinated in a linear coordination geometry to the two nitrogen atoms from different bpp ligands, and the Ag−N bond distances are 2.217(3) Å, as expected for $\mathrm{Ag^I}$ complexes with pyridine-type ligands.[6] The nitrate anions are located at these cavities and in close contact with the $\mathrm{(CH_2)_3}$ groups of the adjacent polymeric chains [C···O 3.428(6)−3.474(5) Å; C−H···O 145.6−165.9°].

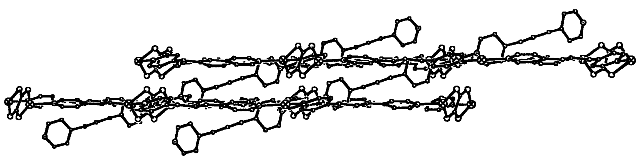

Figure 2. Side view showing 3D pseudo-polyrotaxane in **1**. The nitrate anions are omitted for clarity.

The most interesting structural feature of **1** is that there are two different structural motifs with different dimensions, 1D coordination polymeric chains and 2D layers, and what is important is that the 1D polymeric chains interpenetrate the 2D (6,3) sheets in an inclined fashion to generate a rare 3D pseudo-polyrotaxane (Figure 2). Structures containing interpenetrating nets that have different topology and/or chemical composition are at present rare,[7,8] though the occurrence of interpenetrating polymeric networks, once a rarity, is now becoming increasingly common, aided by the rapid growth of this network-based crystal engineering. Even less common are structures in which networks of different dimensions interpenetrate. A few interesting examples are a structure in which an α-Po-related coordination polymer interpenetrates with hydrogen-bonded 2D (6,3) solvent networks reported by Robson's group,[8a] a structure in which 1D "railroad"-type coordination polymers interpenetrate (4,4) sheets of phenanthrene molecules reported by Zaworotko's group,[8b] a structure with a novel structural motif consisting of stacks of infinite ladders interpenetrated by bundles of infinite chains,[8c] and the most remarkable example, which is that reported by Ciani's group in which 1D coordination ribbons of rings and 2D (4,4) coordination layers interpenetrate in an inclined fashion to generate a rare 3D polycatenane.[3c] Therefore, the rare pseudo-polyrotaxane of **1** generated by different dimensions interpenetrating represents another important new example of uncommon networks of different dimensions interpenetrating.

The structure of **2** consists of an open 3D neutral network of rectangular channels with lattice water molecules. As shown in Figures 3 and 4, the overall network **2** consists of β-sheets and $\mathrm{ox^{2-}}$ ligands as pillars. Each $\mathrm{Ag^I}$ atom, in a T-shaped coordination geometry, is ligated by two ppa units [Ag−N 2.177(4) and 2.187(4) Å] and one relatively weakly coordinated $\mathrm{ox^{2-}}$ counterion [Ag−O 2.641(4) Å]; adjacent Ag−ppa chains are linked into interesting two-dimensional β-sheetlike layers by weak ligand-unsupported Ag···Ag contacts.[6e,f] The Ag···Ag separation of 3.202(1) Å is comparable to those [3.116(1) and 3.286(2) Å] found in two

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[4] Anal. Calcd for $\mathrm{C_{41}H_{42}Ag_3N_7O_7}$ **1**: C, 46.09; H, 3.96; N, 9.18%. Found: C, 45.92; H, 3.92; N, 9.12%. Anal. Calcd for $\mathrm{C_{26}H_{40}Ag_2N_6O_{15}}$ **2**: C, 35.00; H, 4.52; N, 9.42%. Found: C, 34.98; H, 4.46; N, 9.30%. Powder XRD for **1** *d*/Å, *hkl* (intensity): 13.35, 002 (100); 6.68, 004 (20); 6.62, 023 (30); 4.85, 131 (20); 4.75, −132 (20); 4.10, −134 (20); 3.80, 200 (50); 3.55, −221 (30). Powder XRD for **2** *d*/Å, *hkl* (intensity): 12.40, 200 (90); 8.94, −202 (100); 6.64, −402 (20); 6.20, 400 (20); 4.07, −404 (40); 3.74, 221 (40); 3.22, 421 (20); 3.21, −622 (50).

[5] X-ray single-crystal diffraction data collection for **1** and **2** were collected on a Siemens *R*3*m* diffractometer. Crystal data for **1**: monoclinic, space group *C*2/*c*, $a = 7.619(2)$ Å, $b = 19.781(4)$ Å, $c = 26.799(5)$ Å, $\beta = 94.720(10)°$, $U = 4025.2(15)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.763$ g cm^{-3}, μ (Mo Kα) = 15.05 cm^{-1}. R1 = 0.0384, wR2 = 0.0988 (for all data). **2**: monoclinic, space group *C*2/*c*, $a = 28.947(8)$ Å, $b = 8.617(3)$ Å, $c = 16.307(6)$ Å, $\beta = 121.07(1)°$, $U = 3484(2)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.701$ g cm^{-3}, μ (Mo Kα) = 12.00 cm^{-1}. R1 = 0.0513, wR2 = 0.1441 (for all data).

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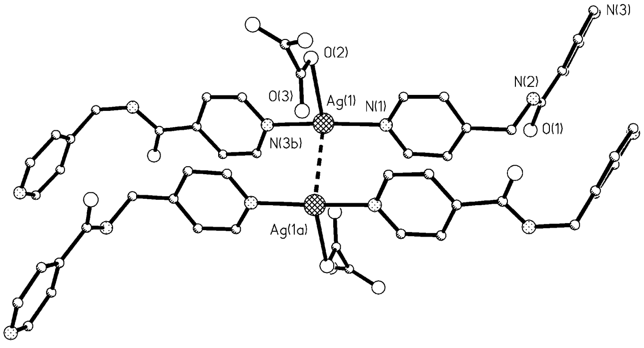

Figure 3. Coordination environments of the metal atoms in **2**.

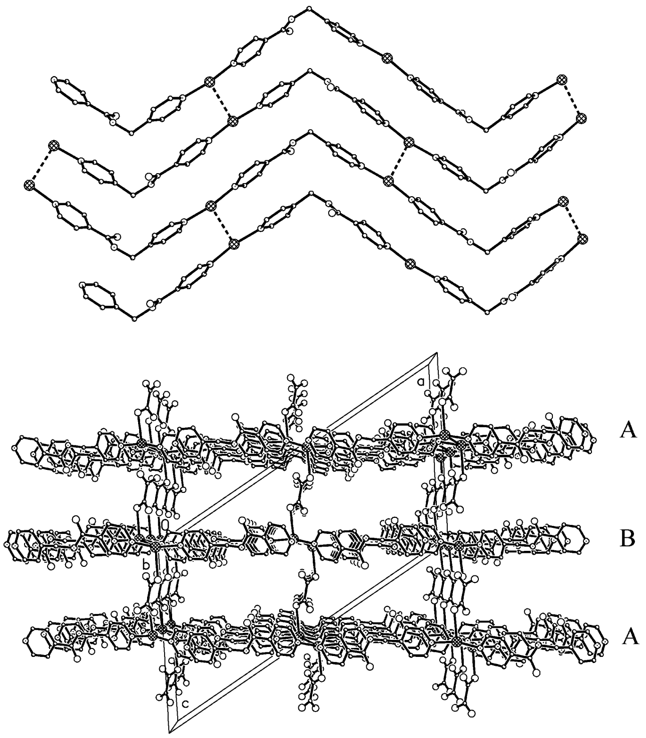

Figure 4. β-Sheetlike layer (top) and 3D coordination network (bottom) viewed from the *b*-axis direction in **2**.

recently reported infinite molecular ladders ([Ag(4,4′-bpy)X], X = $MeCO_2^-$ and $H_2PO_4^-$)[6f] and those [2.970(2)−3.312(1) Å] found in other Ag^I coordination polymers with pyridyl-donor ligands,[3d,6a−e] indicating weak Ag···Ag interaction.[9]

It is noteworthy that in **2** the ligand-unsupported Ag···Ag contacts and side-to-side interchain offset stacking interactions extend the 1D coordination chains into 2D sheets, different from our previously reported results of silver(I)-4,4′-bipy systems,[6f] and from those reported in linear Ag-(4,4′-bpy)X (X = NO_2^-, BF_4^-) and T-shaped [Ag(4,4′-bpy)](NO_3) formed by the related Ag^I salts and 4,4′-bpy.[6a,b] The adjacent layers are interconnected by the ox^{2-} ligands, resulting in a novel 3D network (Figure 4) with rectangular channels (ca. 8.1 × 11.9 Å^2). The lattice water molecules are situated at these channels and stabilized by rich hydrogen-bonding interactions. It should be noted that the different structure types present in **1** and **2** can be ascribed to the fact that the bpp and ppa ligands contain flexible hydrophobic ($(CH_2)_3$) and hydrophilic (CH_2NHCO) spacers, respectively. In **2**, the hydrogen bonding interaction between the hydrophilic CH_2NHCO groups and lattice water molecules may play a role in the orientation of the ppa ligand in the β-sheetlike layers, resulting in a vastly different structural feature.

In summary, we present two fascinating molecular architectures utilizing flexible pyridyl-type ligands containing hydrophobic $(CH_2)_3$ and hydrophilic (CH_2NHCO) spacers. The isolations of **1** and **2** imply that introducing two or more functional anions in a synthetic system may lead to new types of metal coordination polymers with intriguing architecture and topology.

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Supporting Information Available: Two figures (PDF) and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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