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Novel silver(I)–organic coordination polymers: conversion of extended structures in the solid state as driven by argentophilic interactions

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Structurally distinct coordination polymers [Ag(bpp)]ClO_4 1 and [Ag(bpp)]PF_6 2 [bpp = 1,3-bis(4-pyridyl)propane] have been assembled; the conversion of 1 into 2 on treatment with $NaPF_6$ is driven by argentophilic interactions and is the first such transformation reported for silver(I)–organic coordination polymers.

The field of metal–organic coordination polymers[1] has recently attracted intense interest because such supramolecular compounds have potential as smart optoelectronic,[2] magnetic,[3] microporous,[4] and biomimetic materials.[5] The design of coordination polymers takes into account 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 counter ion influence. A subtle alteration in any of these factors can lead to new extended network structures. Thus, a great variety of supramolecular architectures have been ingeniously constructed. These not only have aesthetic appeal, but occasionally exhibit interesting functions. In contrast, there has been a scarcity of information on supramolecular reactivity featuring well-defined conversions of extended structures in coordination polymers.[6] Such transformations may find applications in molecular recognition and chemical sensor technologies. For cationic networks, exchange of anions has recently been reported to induce the interconversion of several silver(I)–polynitrile coordination polymers.[6a] These changes apparently involve the breaking and forming of silver(I)–nitrile coordination bonds, but the driving force and mechanism are not well understood.

The coordination affinity of silver(I) for pyridyl-donor ligands is well known, and the argentophilic d^{10}–d^{10} bonding interactions frequently affect the extended structures of the resulting coordination polymers.[7] The commercially available 1,3-bis(4-pyridyl)propane (bpp) is a bipyridine-type ligand with a flexible –$CH_2CH_2CH_2$– spacer, and several research groups have reported a few Ag^I–bpp cationic networks where the counter ion is $CF_3SO_3^-$ or NO_3^-.[8] Ciani and coworkers have also mentioned that bpp reacts with $AgBF_4$ or $AgClO_4$ in 2:1 molar ratio to form two-fold interpenetrated diamondoid networks.[8a] We have sought to generate novel cationic Ag^I–bpp networks with various counter ions and use such systems for the study of anion-induced transformations of supramolecular structures. Herein we report the assembly of [Ag(bpp)]ClO_4 **1** and [Ag(bpp)]PF_6 **2**, two coordination polymers with novel and distinct cationic network structures. We also describe the well-defined, irreversible conversion of **1** into **2** on treatment with $NaPF_6$. This conversion is unique in that it is driven by forming more and stronger Ag–Ag bonds in the polymeric cation (see below); no such transformations have been previously reported for silver(I)–organic coordination polymers.

Solution-phase reactions of bpp with $AgClO_4$ and $AgPF_6$ in 1:1 molar ratio generate **1** and **2**, respectively.† The structures of **1** and **2** determined *via* single crystal X-ray diffraction analysis‡ are shown in Fig. 1. In both **1** and **2**, each Ag^I ion is coordinated by two pyridyl nitrogen atoms of different bpp units in approximately linear geometry, and the Ag–N bond distances fall between 2.114(5) and 2.144(5) Å, as expected for Ag^I complexes with pyridine-type ligands . Despite this similarity in local silver(I)–pyridyl coordination, **1** and **2** have significantly different extended supramolecular structures due to differences in argentophilic interaction.

In the cationic network of **1**, there are two types of crystallographically and chemically equivalent Ag^I ions, both of which form 1-D sinusoidal chains with the bound bpp molecules where each –$CH_2CH_2CH_2$– spacer adopts a TT conformation.[8a] Adjacent chains containing one type of Ag^I ions are cross-linked through argentophilic bonding to form 2-D layers, as evidenced by the Ag–Ag contact [3.2214(10) Å] that is well below the van der Waals diameter of silver (3.44 Å).[9] The 1-D sinusoidal chains containing the other type of Ag^I ions lack interchain Ag^I–Ag^I interactions because the shortest Ag···Ag separation (4.40 Å) is greater than the van der Waals

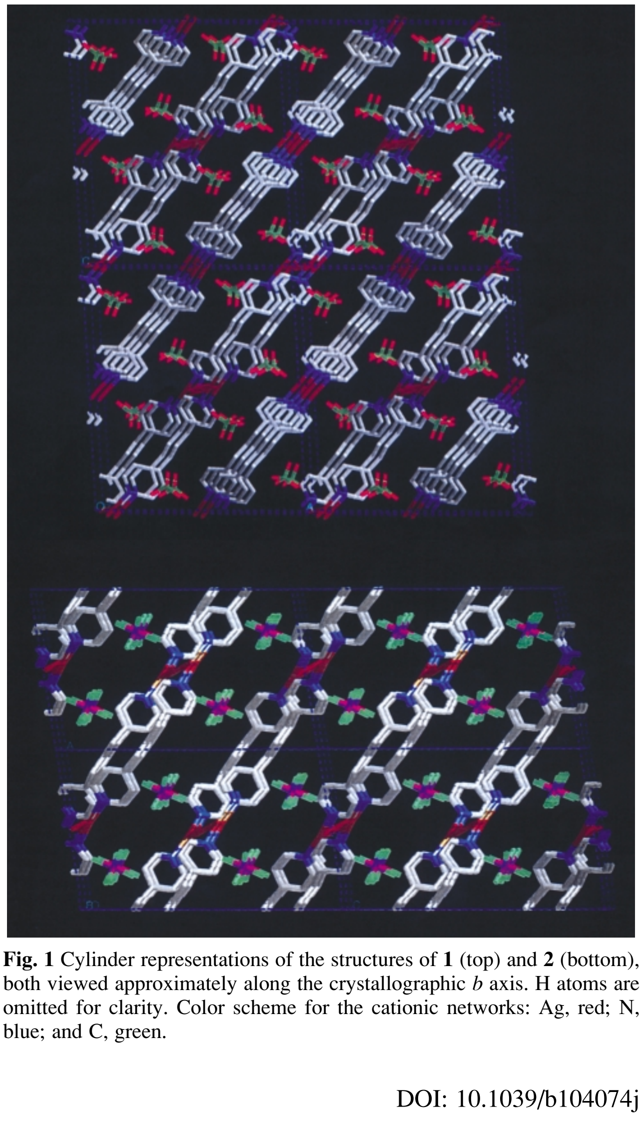

Fig. 1 Cylinder representations of the structures of **1** (top) and **2** (bottom), both viewed approximately along the crystallographic *b* axis. H atoms are omitted for clarity. Color scheme for the cationic networks: Ag, red; N, blue; and C, green.

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diameter. In the entire crystal structure of **1**, the 2-D Ag^I–bpp layers and the 1-D Ag^I–bpp chains pack the space alternately. The ClO_4^- ions occupy the volume between the 2-D layers and 1-D chains, interacting with the cationic network through predominantly ionic bonding, with the shortest Ag···O(ClO_4^-) separation at 2.78 Å. To our knowledge, the polymeric cation of **1**, consisting of stacked 2-D layers separated by 1-D chains, exhibits an unprecedented structural motif in coordination polymers. Structurally, the polymeric cation of **2** is more straightforward than that of **1**. All silver(I) ions are crystallographically and chemically equivalent and are each coordinated by two pyridyl nitrogen atoms of different bpp units. The sinusoidal Ag^I–bpp chains are cross-linked *via* stronger and shorter Ag–Ag bonds [3.0852(9) Å] in comparison with those in **1**. The Ag–Ag bond distance in **2** is comparable to that observed in [Ag(bpy)]NO_3 (bpy = 4,4′-bipyridine).[7e,f] However, adjacent Ag^I–bpy chains are perpendicularly linked to afford a 3-D framework whereas the Ag^I–bpp chains in **2** are connected approximately in parallel to generate a 2-D layer. The known [Ag(bpp)](CF_3SO_3)·EtOH and [Ag(bpp)]NO_3 display wave-like Ag^I–bpp chains similar to **2**, but no interchain Ag–Ag bonds were reported.[8] The 2-D Ag^I–bbp layers in **2** are intercalated by the PF_6^- ions and the interaction between $[Ag(bpp)]^+$ and PF_6^- is predominantly ionic, the shortest Ag···F(PF_6^-) separation being 2.75 Å. In both **1** and **2**, π–π interactions between pyridyl rings are very weak.[10,11]

Comparing the extended structures of **1** and **2**, we reasoned that the latter is more stable than the former primarily because of the greater number and strength of Ag–Ag bonds. This rationale prompted us to study the possibility of transforming **1** into **2** *via* anion exchange. Reaction of **1** with $NaPF_6$ affords **2** in quantitative yield [eqn. (1)]:

$$[Ag(bpp)]ClO_4(s) + NaPF_6(aq) \rightarrow [Ag(bpp)]PF_6(s) + NaClO_4(aq) \quad (1)$$

The IR spectrum of the exchanged solid shows the disappearance of the ClO_4^- bands and the appearance of the intense PF_6^- adsorptions at 835 and 561 cm^{-1}. Furthermore, the X-ray powder diffraction (XRD) pattern of the exchanged solid is identical to that of [Ag(bpp)]PF_6 prepared from $AgPF_6$ and bpp (Fig. 2). According to IR and XRD monitoring, no reaction occurred between **2** and $NaClO_4$ even after a sample of **2** was immersed in a large excess of saturated aqueous solution of $NaClO_4$ (*ca.* 14 M) for five days. This result agrees with the observation that **2** has greater structural stability than does **1**.

In conclusion, we have obtained structurally distinct coordination polymers [Ag(bpp)]ClO_4 and [Ag(bpp)]PF_6. Treatment of [Ag(bpp)]ClO_4 with $NaPF_6$ affords [Ag(bpp)]PF_6, and this reactivity is well-correlated with the extended structures of the two compounds. These findings illustrate the structure–property relationship at the supramolecular level. We are currently attempting to extend this study to silver(I) complexes with other pyridyl-donor ligands.

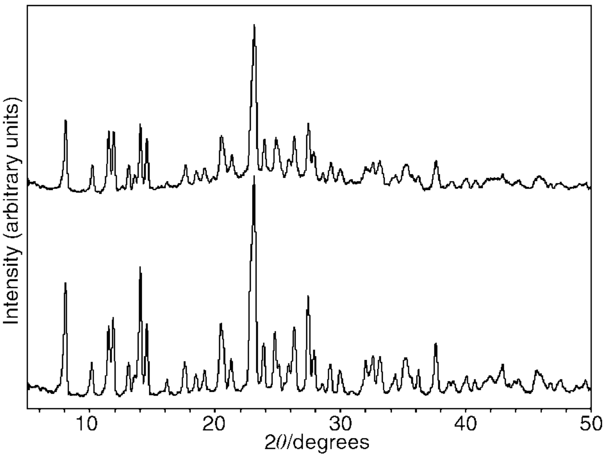

Fig. 2 The XRD patterns of the exchanged solid (top) and [Ag(bpp)]PF_6 prepared from $AgPF_6$ and bpp (bottom).

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Notes and references

† Under ambient conditions, layering of a methanol solution (4 mL) of bpp (0.10 mmol) over aqueous solutions (4 mL) of $AgClO_4$ and $AgPF_6$ (0.10 mmol) produced colorless crystals of **1** and **2** in 51 and 50% yields, respectively. Compounds **1** and **2** are insoluble in water and common organic solvents. The bulk-phase purities of **1** and **2** were confirmed by comparing their observed and simulated XRD patterns. IR (KBr pellet): for **1**: ν/cm^{-1} 2925m, 2858w, 1609s, 1558w, 1500w, 1429m, 1225w, 1097vs, 808s, 626s, 514m. For **2**: ν/cm^{-1} 2923m, 2856w, 1604s, 1558w, 1500w, 1417m, 1069s, br, 835vs, 561s.

‡ *Crystal data*: for $C_{13}H_{14}AgClN_2O_4$ **1**: M = 405.58, monoclinic, space group $P2_1/n$, a = 16.8826(2), b = 8.6694(2), c = 19.9505(2) Å, β = 93.545(2)°, V = 2914.38(7) $Å^3$, Z = 8, D_c = 1.849 g cm^{-3}, T = 173(2) K, μ(Mo-Kα) = 1.583 mm^{-1}, 3568 data with $I > 2\sigma(I)$, $R(F)$ = 0.040.

For $C_{13}H_{14}AgN_2PF_6$ **2**: M = 451.10, monoclinic, space group $P2_1/c$, a = 11.0925(2), b = 8.4883(2), c = 17.6297(4) Å, β = 99.0826(6)°, V = 1639.12(8) $Å^3$, Z = 4, D_c = 1.828 g cm^{-3}, T = 173(2) K, μ(Mo-Kα) = 1.385 mm^{-1}, 2351 data with $I > 2\sigma(I)$, $R(F)$ = 0.0504.

All data were collected on a Siemens P4 diffractometer equipped with a SMART/CCD detector. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. An absorption correction, using SADABS, was applied to the data for **1** while no absorption correction was required for **2**.

CCDC reference numbers 154893 and 154894. See http://www.rsc.org/suppdata/cc/b1/b104074j/ for crystallographic data in CIF or other electronic format.

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