Direction of topological isomers of silver(I) coordination polymers induced by solvent, and selective anion-exchange of a class of PtS-type host frameworks†

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The construction of two types of coordination polymers with closely related 4-connected topologies [PtS and lvt (4^2.8^4)] were achieved based on a well-designed bent dipyrazine linker, and the topological differences only result from the stereochemistry of silver(I) coordination sphere with the same coordination donors. Selective anion-exchange functions of the series of PtS-type coordination networks containing different counter anions (from small BF_4^- to very large SbF_6^-) were identified.

Coordination polymer design and construction is currently a flourishing field of research due to the broad applications as new functional materials.[1] An important aspect of this relatively new chemistry is the analysis and direction of network topologies of the metal–organic frameworks, which is a precondition to make the true and significant development.[2,3] Prediction of coordination polymer topology, however, is still not a trivial exercise at present.[3] Even when organic bridging ligands and metal centers adopt the desired coordination geometries, multiple possible network topologies are available. For example, both the two-dimensional (2-D) (4,4) and the three-dimensional (3-D) NbO networks could be constructed when using square-planar four-connecting nodes.[2a]

On the other hand, reports of the modification of network topology through changing reaction variables such as the counterion or solvent medium have been few but are increasing.[4] In this context, we will describe two types of coordination polymers with differing but closely related network topologies [PtS *vs.* lvt (4^2.8^4)]. Remarkably, in both compounds the ligands adopt identical coordination modes, while the metal atom coordination geometries differ only in stereochemistry (tetrahedral or square-planar nodes) and not in the numbers of ligands or donor atoms they bond to, as observed in all previous cases. This unique change is directed only by the variation of solvent medium/guest, which may promise great advances in crystal engineering. Of further interest, selective anion-exchange function of a series of PtS-type open host frameworks with the inclusion of quite different counter anions (from small BF_4^- to very large SbF_6^-) is identified.

Reaction of 2,5-bis(pyrazine)-1,3,4-oxadiazole (bpzo, see Chart 1) with different AgX salts in $CHCl_3/OH(CH_2)_2OH/CH_3OH$ medium gave **1–4** with general formula $\{[Ag(bpzo)]X\cdot solvent\}_n$ (X = BF_4^-, AsF_6^-, $CF_3SO_3^-$ and SbF_6^-, respectively, and solvent = $1.5H_2O$ for **1**).‡ Alternatively, reaction of bpzo with $AgBF_4$ in CH_3CN medium generated quite unstable crystals of another coordination polymer $\{[Ag(bpzo)](BF_4)_{1/2}(OH)_{1/2}\cdot(CH_3CN)_{1/4}\}_n$ **1a**. Currently, bent building blocks have been relatively less studied in the construction of coordination polymers compared to linear spacers.[5] During our continuous focus on self-assembly of functional metal–organic frameworks with oxadiazole-containing bent linkers,[6] a new ligand bpzo attracted our attention due to its higher possibility of affording unpredictable topologies depending on the abundant potential coordination sites and the biting angle of the chelation function.

The crystal structures of all polymers consist of 3-D open coordination networks and included anions/solvents.§ Complexes **1–4** have the same coordination fashions and network topologies which are, however, different to those of **1a**. The local geometries of both types of structures (Fig. 1) show that each silver atom coordinates to two ligands *via* a single pyrazine nitrogen each, and to two further ligands *via* chelation to a pyrazine nitrogen and an oxadiazole nitrogen on each ligand. Furthermore, the ligand coordination modes in both structures are identical—each ligand coordinates to four silver atoms, two *via* the pyrazine nitrogens *meta* to the oxadiazole ring, and two others *via* chelation of an oxadiazole nitrogen and an *ortho* pyrazine nitrogen each.

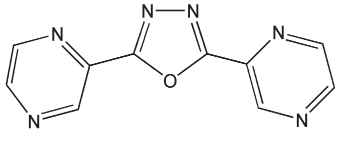

Chart 1

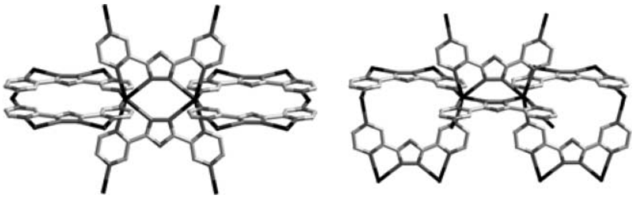

Fig. 1 Local coordination geometries of ligand and metal in the structures of **1–4** (left) and **1a** (right). Bond parameters are listed in Table S1†.

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† Electronic supplementary information (ESI) available: A table of the bond geometries of the silver(I) coordination spheres for all complexes, the color versions of all figures in this communication and anion-exchange experimental procedure and identification of **1–4**. See http://dx.doi.org/10.1039/b508479b

As can be seen (Fig. 1), however, the stereochemical arrangement of the ligands and metals differ in two types of structures. If we focus on two silver atoms in each structure which are connected by a single ligand which chelates to them both (*i.e.* the uppermost ligand in each figure, which connects the two silver atoms in the centre of each figure), then we can see that this pair of silver atoms also coordinates to another bis-chelating ligand, and to four other ligands coordinating to this pair in a monodentate fashion (two per silver atom). In the structures of **1–4**, the two bis-chelating ligands have a *trans* geometry across the disilver pair, while in **1a** the arrangement is *cis* fashion.

Not surprisingly, this diversity in the orientation of the ligands changes the network topology. As each ligand connects to four different silver atoms in a square-planar arrangement, then they can be represented simply as 4-connecting square-planar nodes. Similarly, the silver atoms, which each connects to four ligands, can also be described as 4-connecting nodes. However, while the connectivities of the Ag centers in both types of nets are identical, their geometries are different. In **1–4** the Ag nodes are pseudo-tetrahedral, while in **1a** they are square planar. While, strictly, geometries are irrelevant in true topological analysis, in this case the differing geometries readily explain the different network topologies. The network of **1–4** consists of equal numbers of square-planar and tetrahedral geometries, and thus forms a network with a PtS topology (see Fig. 2 left).[7] The network of **1a** consists of only square-planar nodes, and forms a very rare network with a lvt[3c,8] topology (Fig. 2 right). So far, only nine such metal–organic frameworks have been identified,[3c] six are single[9] and the other three are 2-fold interpenetrated nets.[10]

In each structure the network is cationic, requiring the presence of extra-framework anions, all being disordered to a different extent. These occur in the form of BF_4^-, AsF_6^-, $CF_3SO_3^-$ and SbF_6^-, respectively, for polymers **1–4**. An additional counterion, however, is required in **1a** for charge balance, and for this reason a non-framework oxygen atom found within this structure was assigned as a hydroxide anion rather than water. Half or all of BF_4^- anions in **1** and **1a** lie in Ag_2L_2 windows within the framework created by the bridging of two silver atoms by two ligands coordinating *via* the *meta* pyrazine nitrogens (such as the windows at either side of the central disilver pairs in Fig. 1). Along with the intercalated solvent molecules (water in **1**, and acetonitrile in **1a**), the remaining BF_4^- in **1** and hydroxide counterions in **1a** lie in the infinite square channels running through each structure, which accommodate the larger counter anions in **2–4**. These channels are almost identical,[11] with dimensions of *ca.* 4.1 × 4.1 Å in cross-section (taking into account the van der Waals radii of the channel 'walls'), and run in only one direction (Fig. 3). Note that the solvents and counterions have been removed in this view; in reality, they occupy the channels.

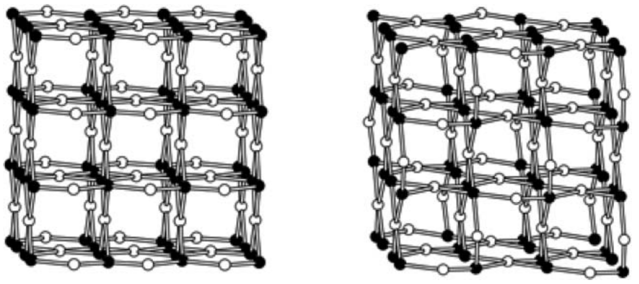

Fig. 2 Network topologies in **1–4** (left, PtS) and **1a** (right, lvt). Silver nodes are represented in black, ligand nodes are white.

Normally, the nature of the anion play a key role in formation of the resultant coordination framework, especially for Ag^I which is known to have a myriad bonding modes and coordination spheres.[4a,4b,5b,12] Polymers **1–4** possess the same rigid PtS open frameworks with a limited variation of the void column tuned by the size of the counteranion,[11] which is, to the best of our knowledge, unique in coordination polymer chemistry.[13] **1–4** are air stable and can retain their crystalline integrity at ambient conditions. Thermogravimetric experiments were carried out to investigate their thermal stabilities and the results indicated that the coordination frameworks of **1–4** remain stable up to 150, 194, 196 and 182 °C, respectively, and finally collapsed beyond that temperature. In order to see if these anions could move in and out the host PtS framework freely, the anion-change properties[14] were investigated and validated using IR spectra, elemental analysis and XRPD (ESI)†. Reversible anion exchanges only occur between **3** and **4**; and **1** and **3**, probably due to the different sizes of the anions. The SbF_6^- anion in **4** could be easily replaced by any one of the other three anions, and the AsF_6^- anion generally acts as a successful aggressor to occupy the channels when reacting with the three other complexes. The smaller sized anions in **1** or **2** could not be exchanged by the largest SbF_6^- ion. Additionally, in the processes from **2** → **3** and **2** → **1** attempted by adding the corresponding excess anion, only partial anion exchange was observed even after longer than usual exposures (normally, the exchange is complete within 8 h and 48 h for the cases of no exchange or partial exchange). These results suggest that this fascinating system may have significant potential for application as new molecular-based functional materials.

In summary, two types of Ag^I coordination polymers with closely related 4-connected topologies (PtS and lvt) were achieved with a well-designed bpzo linker. Complexes **1** and **1a** are a pair of topological isomers sensitive to the variety of solvent medium/guest. The topological differences, from the viewpoint of the structure, only result from the stereochemistry of Ag^I coordination (significantly, both types of Ag^I ions have the same coordination donors or ligands, and are 4-connecting nodes in the network), which is unprecedented. It is difficult to definitively evaluate the practical significance of this observation at this stage, however, we have no doubt of the uniqueness of this phenomenon. On the other hand, interesting selective anion-exchange properties

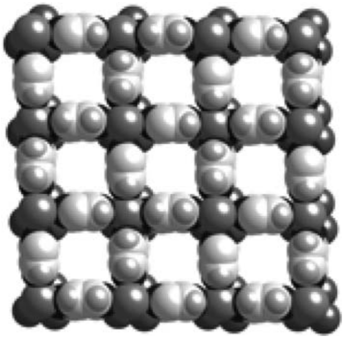

Fig. 3 Space-filling view of the square channels running parallel to *a* axis in **1a**. The structures of **1–4** have similar channels along *c* axis.

in the series of PtS-type coordination networks were also identified, which may provide a new strategy for the conversion of such microporous metal–organic frameworks from laboratory curiosities to practical ion-exchange materials.[15]

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Notes and references

‡ **Synthesis of the new ligand Bpzo.** Pyrazine-2-carboxylic acid (0.15 mol) and hydrazine dihydrochloride (0.08 mol) were mixed with stirring, to which orthophosphoric acid (85%, 50 mL) was added. Then, phosphorus pentoxide (0.48 mol) was carefully added followed by phosphorus oxychloride (0.15 mol) to the above mixture. The viscous solution was heated at 140 °C, with stirring for *ca.* 4 h. After cooling to room temperature, the resultant viscous liquid was poured over distilled water with stirring, dissolved, then neutralized with sodium hydrogencarbonate. A large amount of orange precipitation of bpzo was obtained which was filtered off and dried in air, yield 55%. The recrystallizing procedure could be easily handled from chloroform. ^{1}H NMR ($CDCl_3$): δ = 8.82 (s, 2H) and 9.59 (s, 4H). IR (KBr pellet, cm^{-1}): 1562m, 1434s, 1401s, 1293w, 1159s, 1099s, 1045s, 1018s, 863s, 756s, 528w, 481m. Anal. Calcd for $C_{10}H_6N_6O$ (M_r = 226.20): C, 53.09; H, 2.67; N, 37.14%. Found: C, 53.18; H, 2.71; N, 36.94%. **Preparation of {[Ag(bpzo)]X·solvent}$_n$ (X = BF_4^-, AsF_6^-, $CF_3SO_3^-$ and SbF_6^-, respectively, for polymers 1–4 and solvent = 1.5H_2O for 1).** A CH_3OH solution (5 mL) of AgX (0.2 mmol) was carefully layered onto a buffer of $OH(CH_2)_2OH$ (2 cm), below which a solution of bpzo (0.2 mmol) in $CHCl_3$ (5 mL) was placed in a straight glass tube. Light yellow (for **1**) or colorless (for **2–4**) block-shape single crystals suitable for X-ray diffraction analysis were afforded on the tube wall over 3–5 days in 70%–85% yield. Anal. Calcd for $[Ag(C_{10}H_6N_6O)](BF_4)\cdot1.5H_2O$ (**1**, M_r = 447.91): C, 26.81; H, 2.03; N, 18.75%. Found: C, 26.93; H, 1.75; N, 19.08%. Anal. Calcd for $[Ag(C_{10}H_6N_6O)](AsF_6)$ (**2**, M_r = 523.00): C, 22.96; H, 1.16; N, 16.06%. Found: C, 22.71; H, 1.38; N, 16.20%. Anal. Calcd for $[Ag(C_{10}H_6N_6O)](CF_3SO_3)$ (**3**, M_r = 483.15): C, 27.34; H, 1.25; N, 17.39%. Found: C, 27.18; H, 1.29; N, 17.03%. Anal. Calcd for $[Ag(C_{10}H_6N_6O)]$-(SbF_6) (**4**, M_r = 569.83): C, 21.08; H, 1.06; N, 14.74%. Found: C, 21.42; H, 1.32; N, 14.53%. **Preparation of {[Ag(bpzo)]-$(BF_4)_{1/2}(OH)_{1/2}\cdot(CH_3CN)_{1/4}\}_n$ (1a).** The ligand bpzo (46 mg, 0.2 mmol) was dissolved in CH_3CN (10 mL), to which a CH_3CN solution (10 mL) of $AgBF_4$ (40 mg, 0.2 mmol) was added under stirring for *ca.* 3 min. The resultant solution was filtered and left at room temperature, affording light-yellow block single crystals by slow evaporation of the solvent over 2 weeks. Notably, crystals of **1a** are quite unstable and release the solvents immediately after taken away from the mother liquid (this feature could help us to exclude the crystals of **1** are formed together with **1a**), forming a light yellow amorphous substance (yield based on such materials is 65% and elemental analysis seems to be the desolventized phase, Anal. Calcd for $[Ag(bpzo)](BF_4)_{1/2}(OH)_{1/2}$: C, 31.12; H, 1.70; N, 21.77. Found: C, 31.41; H, 1.49; N, 22.04).

§ Crystal data for **1**: $C_{10}H_9AgBF_4N_6O_{2.5}$, orthorhombic, *Pnnm* (No. 58), a = 10.7833(7), b = 10.9040(7), c = 14.0624(9) Å, V = 1653.47(18) Å^3, Z = 4, μ = 1.280 mm^{-1}, S = 1.067, R = 0.0756 and wR = 0.2006. Crystal data for **1a**: $C_{10.5}H_{7.25}AgB_{0.5}F_2N_{6.25}O_{1.5}$, orthorhombic, *Imm*2 (No. 44), a = 13.856(7), b = 10.659(6), c = 11.177(6) Å, V = 1650.7(15) Å^3, Z = 4, μ = 1.251 mm^{-1}, S = 1.096, R = 0.0624 and wR = 0.1558. Crystal data for **2**: $C_{10}H_6AgAsF_6N_6O$, tetragonal, $P4_2/mnm$ (No. 136), $a = b$ = 10.7675(17), c = 13.994(5) Å, V = 1622.5(6) Å^3, Z = 4, μ = 3.343 mm^{-1}, S = 1.034, R = 0.0394 and wR = 0.1046. Crystal data for **3**: $C_{11}H_6AgF_3N_6O_4S$, tetragonal, $P4_2/mnm$ (No. 136), $a = b$ = 10.7845(19), c = 14.119(5) Å, V = 1642.1(7) Å^3, Z = 4, μ = 1.419 mm^{-1}, S = 1.005, R = 0.0350 and wR = 0.0844. Crystal data for **4**: $C_{10}H_6AgF_6N_6OSb$, tetragonal, $P4_2/mnm$ (No. 136), $a = b$ = 10.8706(19), c = 13.959(5) Å, V = 1649.5(7) Å^3, Z = 4, μ = 2.900 mm^{-1}, S = 1.025, R = 0.0431 and wR = 0.1108. X-Ray diffraction data were collected on a Bruker Smart 1000 CCD diffractometer at 293(2) K. Crystals of **1a** are very sensitive to air and the selected crystal was quickly located in a sealed capillary followed by data collection. The counter anions occupying the channels of the coordination framework in each structure are highly disordered, which have been completely located in the cases of **1**, **1a**, **2** and **4**. For the more complicated $CF_3SO_3^-$ anion in **3**, the SQUEEZE bypass filter of PLATON procedure (P. Van der Sluis, A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 194) was applied to treat regions of diffuse electron density that could not be appropriately modeled. The correction of 296 electrons cell^{-1} for **3** is very close to the required value (318 electron cell^{-1}). CCDC reference numbers 267797–267801. See http://dx.doi.org/10.1039/b508479b for crystallographic data in CIF or other electronic format.

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