Highly Selective Guest Uptake in a Silver Sulfonate Network Imparted by a Tetragonal to Triclinic Shift in the Solid State

Silja K. Mäkinen, Natalia J. Melcer, Masood Parvez, and George K. H. Shimizu*[a]

Abstract: The silver sulfonate network presented herein, silver 3-pyridinesulfonate, reversibly and selectively absorbs MeCN while undergoing a major structural rearrangement. The origin of this structural flexibility is a coupling of the weak coordinating ability of the SO_3 group with the geometrically pliant silver(I) center. Single crystal and powder X-ray structures of both the desolvated and solvated forms are presented in addition to the mechanism of their reversible interconversion. A heterogeneous gas chromatographic study showing selective extraction of the MeCN is also presented. Extended solid frameworks which reorder to any extent are not common but the structure presented herein transforms from a tetragonal to a triclinic crystal system. The results indicate that cooperative interactions in systems based on supposedly weaker interactions can yield softer yet functional networks with behavior unlike that observed in more rigid inorganic frameworks.

Keywords: cooperative phenomena · inclusion compounds · silver · sulfonate ligands · supramolecular chemistry

Introduction

Coordination frameworks exhibiting permanent porosity have now been realized.[1] These compounds couple the functionality of a porous architecture with the structural diversity inherent to coordination compounds. To maintain the integrity of these networks, building units based on strong metal–ligand bonds, such as metal carboxylate[2] or metal phosphonate,[3] are typically employed. An alternative approach would be to employ multiple weaker interactions in a cooperative fashion, one of the hallmarks of supramolecular chemistry.[4] With regards to the assembly of extended networks, cooperative hydrogen bonding has been employed with great success by Ward et al. in their guanidinium sulfonate inclusion family.[5] These softer organic networks have considerable conformational flexibility which leads to extensive inclusion abilities. With respect to inorganic frameworks, it is widely considered that in order for an extended inorganic network to be functional, it must be structurally rigid as with zeolite networks.[6] Inorganic networks coupling stability with flexibility would, in principle, offer an added dimension of functionality to a solid. Our approach to this is to employ more weakly ligating groups and soft metal centers to generate frameworks complementary to purely inorganic solids.

Recently, we,[7] and others,[8, 9] have been interested in studying the flexible coordination of metal sulfonates owing to the weak Lewis basic properties of sulfonate anions. There is a structural analogy of sulfonates with phosphonates although the sulfonates are mono- versus dianionic. Metal phosphonates are an extensively studied class of layered compounds owing to the regular motifs observed for a broad range of phosphonate R group.[3] In these two-dimensional networks, the inorganic component serves as a rigid backbone for the pendent organic groups and has led to materials applications ranging from CO_2 sensors,[10] to photolytic H_2 production[11] to non-linear optical activity.[12] Sulfonate coordination chemistry has been much less studied. With regards to silver(I), a consistently observed trend is that, in a 1:1 assembly, silver sulfonates form layered networks.[7a,b, 8] While these structures are also two-dimensional, the analogy with metal phosphonates does not extend greatly beyond this. Whereas metal phosphonates exhibit very consistent lamellar structures with a broad range of R group, in layered Ag sulfonates, a change as minor as going from benzenesulfonate[7b] to *p*-toluenesulfonate[7a] results in an increased tilt in the R group and a change in the coordination mode of the SO_3 group from η^6 to η^5. Each individual sulfonate interaction is weaker, however, the overall network stability is determined via cooperative bonding of the multiple coordinating sites on each -SO_3 group yielding very stable systems.[13] To compare the ligating properties of these two functional groups, a

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[a] Prof. Dr. G. K. H. Shimizu, S. K. Mäkinen, N. J. Melcer, Dr. M. Parvez
Department of Chemistry, University of Calgary
2500 University Drive N.W.
Calgary, Alberta T2N 1N4 (Canada)
Fax: (+1) 403-289 9488
E-mail: gshimizu@ucalgary.ca

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phosphonate can be thought of as "nailing" an organic group to the inorganic layer. For the -SO_3 group, a more accurate portrayal would be to adhere the organic group to the inorganic layer with a "ball of Velcro" in light of the multiple, weaker interactions with the metals and the roughly spherical shape of the SO_3 group.

The current work presents a silver(I) sulfonate network incorporating both strong Ag–pyridine interactions and weaker Ag–sulfonate interactions in forming an extended network. The result is a three-dimensional framework capable of sorbing and desorbing MeCN in a highly selective fashion. Remarkably, this occurs despite the network requiring major structural rearrangement (*tetragonal* to *triclinic* crystal systems) to take up the sorbate. The flexibility of the framework stems from the combination of the weaker interaction of sulfonates with metal ions and the inherent pliant coordination sphere of silver(I), a d^{10} metal ion with no crystal field stabilization energy.[14] Single crystal structures and thermal analysis of both the dense and solvated forms of the complex are reported. In addition, PXRD data showing the sorption phenomenon, and a GC experiment to illustrate both selectivity and that dissolution, as a mechanism for MeCN uptake, is not occurring, are presented.

Results and Discussion

3-Pyridinesulfonic acid and Ag_2CO_3 were suspended in a 2:1 molar ratio in methanol and sonicated for 20 minutes. Over this time, CO_2 gas evolved as the CO_3^{2-} was converted to carbonic acid and the green color of Ag_2CO_3 changed to that of the saturated white product. Diffusion of isopropyl ether into a MeOH solution of the product gave small cube-like crystals of $[Ag(3\text{-}pySO_3)]_\infty$, **1**, suitable for a CCD X-ray analysis. PXRD confirmed that this single crystal material was representative of the phase of the bulk solid. Diffusion of ethyl acetate into a MeCN solution of the white product gave prismatic crystals of $[Ag(3\text{-}pySO_3)(MeCN)_{0.5}]_\infty$, **2**, suitable for an X-ray analysis.

The silver complexes presented herein are a result of two competing structural tendencies. Silver sulfonates have a strong predisposition to form layered networks.[8a,b, 9] For monodentate pyridine-based ligands with silver(I), the most typically observed coordination mode is a 2:1 linear complex.[15] The ligand, 3-pyridinesulfonate (**L**) presents both pyridine and sulfonate moieties within the same monoanionic unit.[16] Thus, if the linear coordination of the pyridine groups is to be satisfied, only a single other silver ion could be present to interact with the two sulfonate groups. This would exclude the 1:1 silver sulfonate ratio observed in layered structures. The result is an alternative framework constrained by the mismatch of these competing structural motifs.

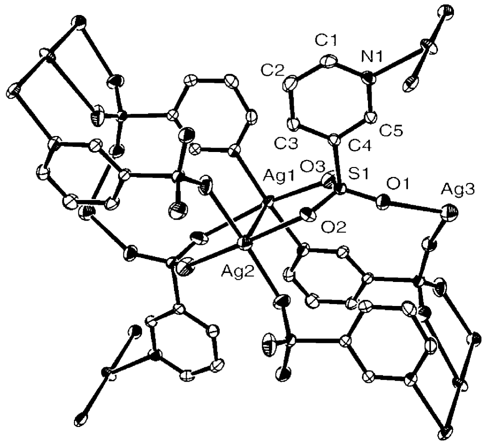

Figure 1. ORTEP plot of structure **1** showing the complex bridging mode of the ligand. The asymmetric unit is labeled. Ellipsoids of 35 % probability are shown. The *c* axis runs parallel to the Ag1−Ag2 contact.

Structure 1, $[Ag(3\text{-}pySO_3)]_\infty$: The structure of the dense form of the network, compound **1**, is a three-dimensional solid containing ribbons of silver ions. The asymmetric unit of this structure consists of one equivalent of silver(I) ions, spread over three sites in a 2:1:1 ratio, and a single type of monoanionic 3-pySO_3 molecule (Figure 1). Ag1 occupies 50 % of the silver sites and is the only silver center which forms bonds to the N atom of the pyridine moiety. The coordination sphere about Ag1 is a highly distorted tetragonal geometry comprised of two *trans* pyridine N donors (Ag1−N1 2.143(2) Å), two weakly interacting *trans* sulfonate oxygen atoms (Ag1−O3 2.710(2) Å), and even longer contacts to two adjacent silver centers (Ag1−Ag1 2.9878(7) Å, Ag1−Ag2 3.0148(4) Å). Ag2, which occupies 25 % of the silver sites, has a less distorted tetragonal geometry comprised of four equivalent sulfonate oxygen atoms in an equatorial plane (Ag2−O2 2.377(2) Å) and axial contacts to two Ag1 centers with the previously quoted distance. Ag1 and Ag2 form the ribbons of silver ions permeating this structure along the crystallographically unique *c* axis in the tetragonal geometry (Figure 2). The metals centers repeat in a Ag1-Ag2-Ag1 unit, as there are twice as many Ag1 centers, with distances shorter than the sum of the van der Waals radii (3.44 Å).[17] Ag3, which occupies the final 25 % of silver sites, is tetrahedrally coordinated by four equivalent sulfonate oxygen atoms (Ag3−O1 2.380(2) Å). These atoms, along with the ligands, form a square arrangement, surrounding each Ag1-Ag2-Ag1 ribbon, down the *c* axis. Overall, the coordination mode of the

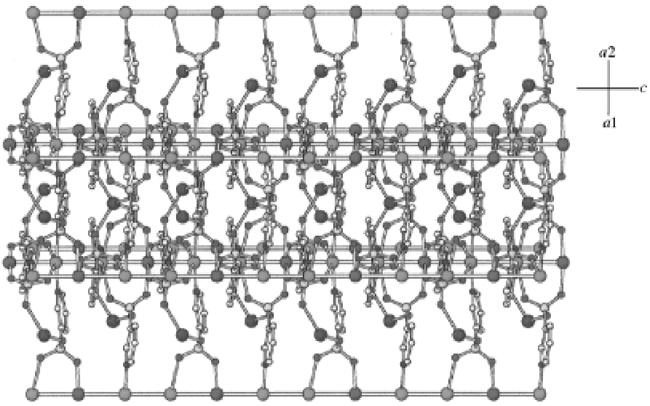

Figure 2. View perpendicular to the unique *c* axis, between the two *a* axes, in the tetragonal structure of **1** with parallel ribbons of Ag ions permeating the structure. Large spheres all represent silver but crystallographic equivalents are shaded differently.

ligand can be described as η^4,μ^4 as each O and N atom forms a single bond to a different silver center. Two sulfonate oxygen atoms, O1 and O3, and the pyridyl N atom form the coordinating "sleeve" for the Ag1-Ag2-Ag1 ribbon. Crystal data are summarized in Table 1. Selected bond distances and angles are shown in Table 2.

Structure 2, $[\mathbf{Ag(3\text{-}pySO_3)(MeCN)_{0.5}}]_\infty$: The structure of $[Ag(3\text{-}pySO_3)(MeCN)_{0.5}]_\infty$, **2**, is comprised of linked 24-membered rings (Figure 3). Ag(pyridine)$_2$ units in a distorted linear geometry (Ag1–N1 2.148(5) Å, Ag1–N2 2.161(5) Å, $\sphericalangle$N1-Ag-N2 = 164.3(2)°) form the top and bottom borders of each ring and the sides are comprised of SO_3^- groups bridged by a second silver center, Ag2. The coordination sphere of Ag2 is a distorted tetrahedron comprised of three oxygen atoms, from three different sulfonate groups, and a molecule of MeCN (Ag2–O1 2.455(6) Å, Ag2–O5 2.333(5) Å, Ag2–O6 2.318(4) Å, Ag2–N3 2.203(6) Å). The rings have approximate dimensions 7.9(1) Å high by 14.6(1) Å wide, defined by the transannular Ag–Ag distance, as oriented in Figure 3. The MeCN molecules bound to Ag2 are situated on opposite sides of the plane of the ring. The 24-membered rings orient along the *c* axis to form channels. Each channel is occupied by two MeCN molecules, bound to an Ag2 atom from an adjacent 24-membered ring. The extended packing of the structure (Figure 4) reveals that the 24-membered rings are

Table 1. Crystal data and refinement summaries for structures **1** and **2**.

Formula	$C_{20}H_{16}N_4O_{12}S_4Ag_4$ (**1**)	$C_{12}H_{11}N_3O_6S_2Ag_2$ (**2**)
M_w	1064.09	573.10
crystal system	tetragonal	triclinic
space group	$I\bar{4}$	$P\bar{1}$
a [Å]	12.3336(5)	10.373(4)
b [Å]	12.3336(5)	11.252(5)
c [Å]	9.0174(5)	8.123(3)
α [°]	90	105.43(4)
β [°]	90	112.22(3)
γ [°]	90	89.70(3)
V [Å^3]	1371.71(11)	841.3(5)
Z	2	2
ρ_{calcd} [g$^{cm^{-3}}$]	2.576	2.262
μ [mm^{-1}]	3.190	2.58
crystal dimensions [mm^3]	0.28 × 0.22 × 0.11	0.30 × 0.19 × 0.08
λ [Å]	0.71073	0.71073
θ range [°]	2.34 to 30.48	2.69 to 25.05
reflections	1788 $I > 4.0\sigma I$	1973 $I > 3.0\sigma I$
total unique reflections	2086	2993
total measured reflections	5889	3171
R [$I > 2\sigma(I)$]	0.0231	0.031
Rw	0.0451	0.032
goodness of fit	0.855	1.36
last D-map [e Å^3]		
deepest hole	−0.568	−0.540
highest peak	0.411	0.530

$R_f = (\Sigma(F_o - F_c)/\Sigma(F_o)$, $Rw = (\Sigma\omega(F_o - F_c)^2/\Sigma\,\omega(F_o)^2)^{0.5}$.

Table 2. Selected bond lengths and angles for structure **1**.[a]

Bond	Length [Å]	Bond	Length [Å]
Ag1–N1	2.143(2)	Ag1–Ag1	2.9878(7)
Ag2–O2	2.377(2)	Ag1–Ag2	3.0148(4)
Ag3–O1	2.380(2)	Ag1–O3	2.710(2)
S1–O1	1.439(2)	S1–O2	1.436(2)
S1–O3	1.442(2)		
Bond	**Angle [°]**	**Bond**	**Angle [°]**
N1-Ag1-N1a	172.4(2)	N1-Ag1-Ag1a	86.21(8)
N1-Ag1-Ag2	93.79(8)	Ag1-Ag1a-Ag2	180.0
O2-Ag2-O2a	174.8(2)	O2-Ag2-O2b	90.12(1)
O2-Ag2-Ag1	92.62(9)	O2b-Ag2-Ag1	87.38(9)
Ag1-Ag2-Ag1a	180.0	O1-Ag3-O1a	104.73(6)
O1b-Ag3-O1a	119.4(1)	O3-Ag1-N1	89.15(8)
O3-Ag1-O3a	157.1(1)	O3-Ag1-Ag1a	101.5(1)
O3-Ag1-N1	92.35(8)	O3-Ag1-Ag2	78.54(8)

[a] Symmetry transformations used to generate equivalent atoms: No. 1: $-x+2, -y+2, z$; No. 2: $y, -x+2, -z$; No. 3: $x+½, y+½, z+½$; No. 4: $-x+3/2, -y+3/2, z+½$; No. 5: $-y+3/2, x+½, -z+½$; No. 6: $y+½, -x+3/2, -z+½$; No. 7: $y, -x+2, -z+1$; No 8: $y-½, -x+3/2, -z+½$; No. 9: $-x+1, -y+2, z$: No. 10: $x-½, y-½, z-½$.

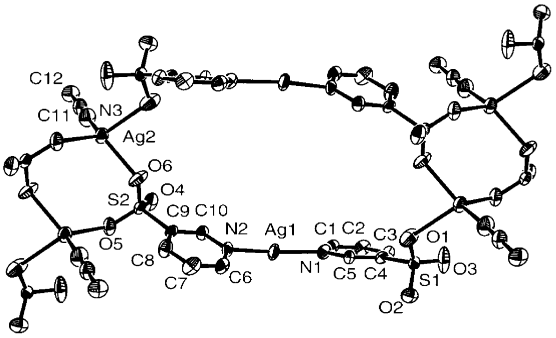

Figure 3. ORTEP plot with labeling scheme showing the 24-membered rings of structure **2** linking to the eight-membered rings. Thermal ellipsoids of 50% probability are shown. Note the *anti* orientation of the MeCN molecules.

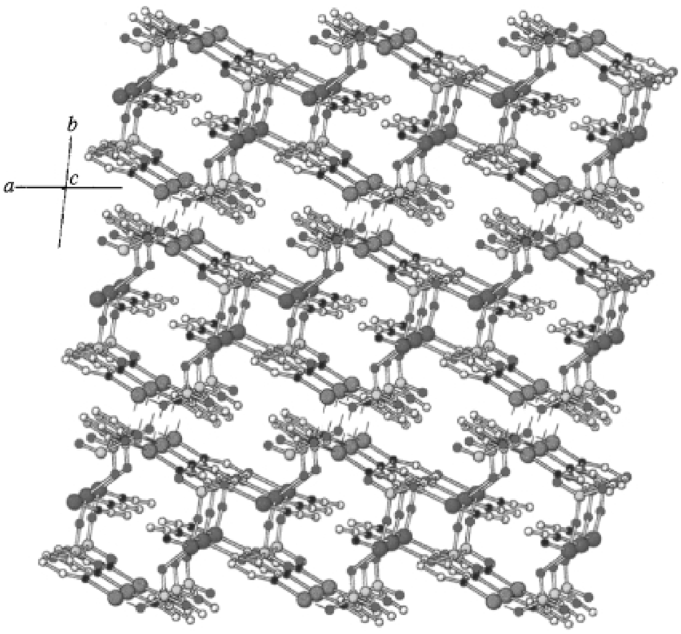

Figure 4. View of the extended structure of **2** down the *c* axis, showing the linking of the 24-membered, MeCN-filled channels by the eight-membered rings. Large spheres all represent silver but crystallographic equivalents are shaded differently.

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cross-linked down the *a* axis, by the previously mentioned Ag2–O5 interaction, to form smaller eight-membered rings. There is also a weak interaction between Ag1 and O6 (Ag1–O6 2.619(3) Å) which links the channels in the *b* direction. This interaction, coupled with the constraints of forming the 24-membered ring, results in the distorted linear geometry of Ag1. Crystal data are summarized in Table 1. Selected bond distances and angles are shown in Table 3.

Table 3. Selected bond lengths and angles for structure **2**.[a]

Bond	Length [Å]	Bond	Length [Å]
Ag1–N1	2.146(6)	Ag1–N2	2.160(6)
Ag2–N3	2.204(7)	Ag2–O1	2.455(6)
Ag2–O5	2.333(5)	Ag2–O6	2.318(5)
S1–O1	1.437(6)	S1–O2	1.450(6)
S1–O3	1.427(6)	S2–O4	1.436(5)
S2–O4	1.449(5)	S2–O4	1.454(6)
Bond	**Angle [°]**	**Bond**	**Angle [°]**
N1-Ag1-N2	164.2(2)	N3-Ag2-O6	125.6(3)
N3-Ag2-O5	114.3(2)	O5-Ag2-O6	106.7(2)
N3-Ag2-O1	105.5(2)	O1-Ag2-O6	84.0(2)
O1-Ag2-O5	117.8(2)		

[a] Symmetry transformations used to generate equivalent atoms: No. 1: $-x, -y, -z$.

Interconversion of structures 1 and 2: Significantly, structures **1** and **2** can be interconverted by the reversible sorption and removal of MeCN. Differential scanning calorimetry (DSC)/thermogravimetric analysis (TGA) of **2** gave a baseline signal to 170 °C at which point loss of the MeCN molecules (7.26% of sample weight) was observed. No further transitions were observed until 320 °C at which point an irreversible endothermic transition, associated with the sample turning black, was observed. In a study of layered networks, we have observed loss of Ag^I-bound MeCN at 95 °C (cf. b.p. (MeCN) 82 °C).[18] The observed value of 170 °C in **2** for loss of MeCN indicates the solvent molecules are tightly bound by the framework and that there are likely significant stabilizing interactions with the surrounding channel. PXRD of the desolvated structure showed that the sample was identical to structure **1**. Structure **1** would reabsorb MeCN and convert to structure **2** if left in contact with MeCN vapor over a period of 10–14 days. Alternatively, treatment of **1** with a small drop of MeCN while in the PXRD sample holder very rapidly (the time required to start the PXRD) converted the structure to **2**. This requires a major reorganization required on the part of the network as shown in the shift of tetragonal unit cell parameters for **1**, and triclinic for **2**. Figure 5 shows the interconversion of the two structures as monitored by PXRD. The solvation/desolvation cycle was repeated twenty times with complete framework integrity.[19]

The *tetragonal* to *triclinic* structural rearrangement exhibited by **1** to form **2** is quite remarkable. From the perspective of a purely inorganic network, it is difficult to perceive a framework reordering to such an extent although thermal phase transitions between *monoclinic* and *orthorhombic* crystal systems have been observed in zeolite-like solids.[20] Coordination networks with "sponge-like" properties (i.e., they swell to incorporate guest molecules), incorporating flexible organic linkers, have also been reported.[21] However, we are aware of only a few examples where the origin of this flexibility is the actual metal coordination sphere and the ligand interaction.[22–26] Cariati et al. have reported a Cu-iodide structure with 4-picoline that converts between a one-dimensional step-polymer and a cubane tetramer upon toluene inclusion.[22] This requires a *monoclinic* to *tetragonal* shift, however, the extended structure is not maintained. Long et al. have reported an infinite network of Re-chalcogenide clusters bridged to Co^{II} by cyano groups.[23] These authors demonstrate vapochromic behavior, after loss of water, stemming from an octahedral to tetrahedral rearrangement of the Co centers in the solid state. Selectivity of guest uptake is also observed in this case, however, the structure of the desolvated network was not determined. Ciani et al. have reported a Cu^I 1,2,4,5-tetracyanobenzene extended network which loses THF to rearrange from a *monoclinic* form to a more dense *orthorhombic* form.[24] Reversibility of the process was not facile as immersion of the desolvated material in THF(l) for a week was required. It should be noted that, of these three structures, two contain Cu^I, another d^{10} ion, and the third contains Co^{II}, which has the lowest ligand field energetic preference for octahedral versus tetrahedral geometry. Finally, Ripmeester and Soldatov have performed very thorough work on a Cu^{II}-acetylacetonate derivative which converts, with guest inclusion, between a porous cyclic hexamer structure and a dense phase of discrete complexes.[25]

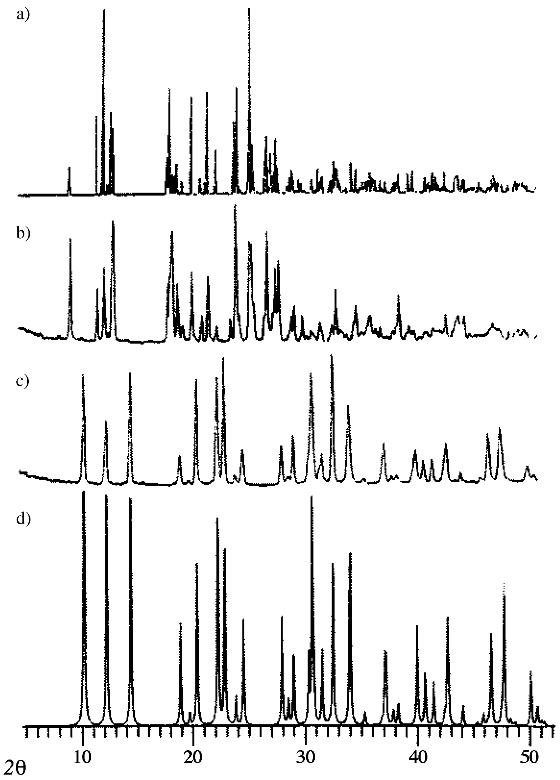

Figure 5. Powder X-ray diffraction patterns illustrating the interconversion of **1** and **2**. a) Simulated PXRD of structure **1** from the single-crystal data. b) The desolvated framework, identical if obtained directly on a sample of **1** or, as shown, by desolvating **2**. c) **1** immediately (ca. 5 s) after treatment with a drop of MeCN while in the PXRD sample holder, showing conversion to **2**. d) Simulated PXRD of **2** based on the single-crystal data.

The linking interaction in this example is a Cu–methoxy O bond which is cleaved in going from the porous (*trigonal*) from to the dense (*orthorhombic*) form. None of the structures discussed above undergoes the extent of structural rearrangement (tetragonal crystal system to triclinic) observed in the present work while maintaining a connected extended structure.

A mechanism for the interconversion of structures **1** and **2** may be proposed based upon a comparison of the two single crystal structures. Structure **2** contains two types of Ag ion in a 1:1 ratio, those sulfonate-ligated and those pyridine-ligated. Upon removal of the MeCN from **2**, the structure collapses to fill the void space which would otherwise exist. The Ag–O interactions, ranging from 2.310–2.619 Å, would be expected to cleave rather than the stronger Ag–pyridine bonds (Ag–N 2.148–2.161 Å). Figure 6a is a view of structure **2** where the MeCN molecules in the lower half have been artificially deleted. The proposed mechanism of conversion may be considered very much like the collapse of a cardboard square by bending one side to force it into the box's cavity. The rearrangement begins with the "folding in" of one of the sulfonate-ligated silver ions, the side of the square, to fill the void generated by the loss of MeCN. This places this Ag ion in proximity to the pyridine bound silver ions. This motion would necessitate the translation of the second, originally equivalent, sulfonate-ligated silver ion in the same direction but away from the void (out of the square) to generate a third type of Ag center in the framework. Figure 6b shows a view of structure **1** along the diagonal between the *a* and *b* axes. As described earlier in this article, three different types of silver ion are observed in **1** in a 2:1:1 ratio, twice as many pyridine-ligated silver centers being present as each sulfonate-ligated. This is exactly the ratio which would result from the proposed rearrangement mechanism. Furthermore, Figure 6b shows that one of the sulfonate-ligated silver centers is now in proximity (ca. 3.0 Å) from the pyridine-ligated silver ions and that the other sulfonate-ligated silver ion is folded away from the pyridine-ligated silver centers. This is again, exactly as would be anticipated based on the proposed mechanism. Significantly, in order for the network to rearrange in the manner proposed, only weak Ag–O interactions need be broken. This occurs as the sulfonate group rotates and new Ag–O interactions form. None of the stronger Ag–N bonds is cleaved.

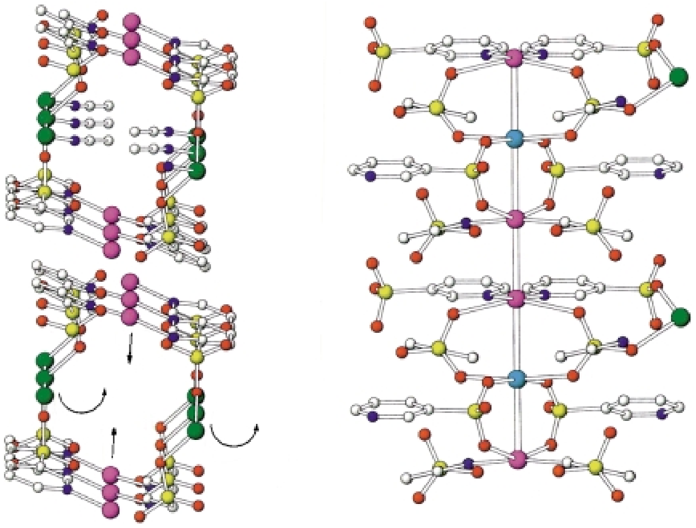

Figure 6. Illustration of the mechanism of interconversion of a) structure **2**, on the left, to b) structure **1**, on the right. MeCN molecules have been artificially deleted in **2** to illustrate the void which would exist. Large spheres all represent silver but the crystallographically equivalents are colored differently (pink, green, turquoise) to indicate this.

In this example, two factors contribute to the ability of the network to rearrange. Firstly, the "ball of Velcro" coordination of the sulfonate group allows the compromise of one weak Ag–O interaction while a new Ag–O interaction forms, enabling a reasonable continuum of silver ion ligation by the sulfonate oxygen atoms. Secondly, silver(I) itself is notorious for having a pliant coordination sphere stemming from its d^{10} electronic configuration. Therefore, no single geometry is overwhelmingly energetically favored.[14]

Selectivity of inclusion: In the above PXRD experiments, it was noted that if propionitrile or butyronitrile was substituted for MeCN in the above procedures (i.e., wetting and vapor diffusion), the PXRD indicated no change from structure **1**. TGA analysis of these same compounds, revealed the loss of the nitrile at the boiling point of the pure solvent, and indicated no interaction with the network. The implication of these observations was that structure **1** was selective for the uptake of MeCN. To further verify this observation, an experiment was performed where the desolvated compound, **1**, was suspended in a solution of mixed nitriles in tetradecane. Tetradecane was chosen as **1** had no solubility in this solvent and did not interfere with detection of the other analytes via gas chromatography. The purpose of this experiment was twofold. In addition to confirming that structure **1** was indeed selective for the sorption of MeCN over other nitriles, the experiment would verify that the observations in the PXRD did correspond to a structural change with sorption rather than a dissolution/recrystallization event.

A sample of the desolvated complex, **1**, was treated with a mixture of two equivalents of each of acetonitrile, propionitrile, butyronitrile, and hexanenitrile, as a 10% total solution in tetradecane to prevent dissolution, and analyzed by gas chromatography. The results of the GC experiments confirmed the resorption of MeCN and also quantified the selectivity of the phenomenon. The process occurred with complete selectivity over butyronitrile and hexanenitrile, and a 2.25:1 selectivity over propionitrile. In the absence of acetonitrile, propionitrile is not taken up by the framework. Given the connectivity of the framework, many channels would open simultaneously in the presence of MeCN and under this circumstance, propionitrile is included.[27] Given the fact that MeCN and EtCN contain identical functionality and differ by only a methylene group, this level of selectivity is remarkable. Other solvents which afforded no change in the PXRD of **1** were THF, benzene, EtOH and even MeOH.

Conclusion

While a rigid coordination network displaying permanent porosity is undoubtedly appealing,[1] framework flexibility is a quality zeolite-like networks do not possess and this softer class of solids may provide a complementary approach to porous materials. The present work shows a robust network ($>300\,^{\circ}C$) which is able to rearrange to accommodate MeCN with high selectivity despite relying on weakly ligating sulfonate groups.

In a general sense, this complex illustrates the promise of network structures based upon weaker interactions. In a recent Concepts paper, Kahn discusses the potential of designing novel magnetic materials based upon flexible coordination frameworks.[28] In these materials, magnetism would be regulated by reversible structural changes in the network. Each form, as brought on by guest inclusion, would allow a different degree of spin–spin interactions. The use of more weakly interacting groups in the generation of extended inorganic frameworks may, at first, seem counterintuitive. However, as shown, the resulting structures are not simply less stable analogues, but rather, a different type of framework with properties unlike those observed in more rigid structures.

Experimental Section

General procedures and instrumentation: Powder X-ray diffraction data were collected on a Scintag SDX2000 powder diffractometer in the Geology and Geophysics Department at the University of Calgary. DSC and TGA were performed on a Netzsch 449C simultaneous thermal analyzer under a nitrogen atmosphere. Gas chromatography was performed on a Hewlett–Packard 5971A GC/MSD. All chemicals were purchased from Aldrich Chemical Company and used as received.

Synthesis of silver 3-pyridinesulfonate, Ag(3-PySO$_3$): Ag_2CO_3 (0.276 g, 1.0 mmol) and 3-pyridinesulfonic acid (0.318 g, 2.0 mmol) were added to methanol (25 mL), the pale green mixture was sonicated in an ultrasonic bath for 20 min. During the reaction, CO_2 gas was found to evolve, and the powder changed color from the original green of Ag_2CO_3 to white. The precipitate was filtered and washed with methanol. The methanol solutions were evaporated to yield further white solid. Both white solids were found to be identical and were identified as $[Ag(3\text{-}PySO_3)]_\infty$, **1**. Combined yield: 0.518 g (97.5%). elemental analysis calcd (%) for: C 22.57, H 1.52; found: C 22.50, H 1.55; FT-IR data (KBr): $\tilde{\nu} = 3033$ (w), 3020(w), 2364 (m), 1585(m), 1418(m), 1229 (s), 1200(s), 1142(m), 1047(s), 1011(s), 807(m), 749 cm^{-1}(m). Colorless single crystals of $[Ag(3\text{-}PySO_3)]_\infty$, **1**, were grown from a MeOH solution by diffusion of isopropyl ether. Colorless single crystals of $[Ag(3\text{-}PySO_3)(MeCN)_{0.5}]_\infty$, **2**, were grown from a MeCN solution via diffusion of ethyl acetate.

General X-ray crystallography: Crystals were selected under an optical microscope, coated in oil and frozen onto a glass fiber. Data for $[Ag(3\text{-}PySO_3)]_\infty$, **1**, were collected on a Bruker SMART APEX CCD diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) using the ω scan mode ($3^{\circ} < 2\theta < 57.3^{\circ}$). The structure was solved by direct methods and refined by full-matrix least squares, based on F^2, using SHELXTL.[29] Data for $[Ag(3\text{-}PySO_3)(MeCN)_{0.5}]_\infty$, **2**, were collected on a Rigaku AFC6S diffractometer using the ω-2θ scan mode ($3^{\circ} < 2\theta < 50.1^{\circ}$) and solved using the teXsan software program.[30] For both structures, silver and sulfur atoms were located first and the remaining atoms found by difference Fourier maps. All non-hydrogen atoms were refined anisotropically. For **1** and **2**, relevant crystallographic data and selected bond distances and angles are shown in Tables 1 and 2, respectively.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-164218 (**1**) and CCDC-133086 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

GC Experiment: Equimolar amounts of acetonitrile, propionitrile, butyronitrile, and hexanenitrile, corresponding to two equivalents per binding site of MeCN (1.0 equiv with respect to total Ag), were mixed in tetradecane to make a 10% solution. This mixture was treated with dried **1** for 15 minutes and rapidly filtered. A standard mixture was prepared and treated in a similar manner to ensure no solvent losses were due to evaporation. GC analysis showed a significant loss of the MeCN signal. Comparable results were obtained using one molar equivalent of the nitriles per Ag binding site (0.5 equiv with respect to the total amount of Ag). As it turned out that it was difficult to accurately integrate the MeCN peak after sorption in this experiment, the results were quantified based upon the experiment employing two equivalents of nitrile per binding site.

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