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Highly Selective Intercalation of Primary Amines in a Continuous Layer Ag Coordination Network

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Layered networks, in the broadest terms, represent an extensively studied family of solids. Fundamental issues with regard to any such network are the stability of the layers, the nature of the groups lining the interlayer region, and the accessibility of the interlayer region, as these items will ultimately define the chemistry of the solid. While maintaining the common two-dimensional motif, the compositions of these solids have varied tremendously, ranging from wholly inorganic aluminosilicate clays,[1] to hybrid inorganic−organic solids (such as metal phosphonates, $M^{n+}(RPO_3^{2-})_{n/2}$,[2] or metal sulfonates, $M^{n+}(RSO_3^-)_n$),[3] to metal−organic coordination solids,[4] to organic solids (such as the H-bonded guanidinium sulfonates).[5]

Hybrid inorganic−organic solids are composed of layers of metal ions bridged by organic derivatives of strongly bonding oxo anions. The layers are continuous and the interlayer is defined by pendant organic groups. In contrast, for the majority of two-dimensional metal−organic coordination solids, the organic units are integral components of the layers. A further notable difference is that the layers in coordination solids are rarely continuous but have some form of open grid structure, typically square[6] or hexagonal.[7] Thus, phenomena often associated with more strongly bonded layered species, such as intercalation and layer swelling,[8] are less observed as possible intercalates can simply move through the grid. There are a number of exceptions to this general statement.[9] A second issue for a metal−organic solid

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is that the interaction of a Lewis basic guest with the host could be of strength comparable to that of the interactions sustaining the host itself leading to more pronounced structural changes or even dissolution.[10] In this light, the observation of intercalation phenomena would provide significant insight into the stability of a layered solid. Efficient intercalation has applications in separations and adsorbent technology, particularly if selective.[11]

We present, herein, a new layered coordination solid, [Ag-(**L**)], **1**, where **L** = 4-pyridinesulfonate. The layers in **1**, like a hybrid inorganic−organic solid, have a continuous rather than open grid structure, however, in contrast, the organic units are incorporated into the layer itself, as in coordination solids. Notably, given the perception of sulfonates as poor ligands,[12] the layers are robust and remain intact even in the presence of an equivalent of Lewis basic amine intercalates. This intercalation is highly selective for primary > secondary ≫ tertiary amines as well as versus other functional group containing molecules. It is also reversible to generate the parent host upon heating.

Silver 4-pyridinesulfonate, **1**, was prepared in one step from Ag$_2$CO$_3$ and 4-pyridinesulfonic acid.[13] Crystals of **1** were grown by slow diffusion of butyl ether into a very dilute solution of **1** in MeOH.[14] Compound **1** has an infinite two-dimensional structure composed of neutral layers as shown in Figure 1. The layers can be described as bricks of [Ag(**L**)$_2$]$^-$ units cross-linked both horizontally and vertically by Ag$^+$ ligation to the sulfonate groups. Two types of silver ion are present in equal ratios; those which coordinate in a linear fashion to the pyridine moieties (Ag1−N1 = 2.163-(3) Å), and those which bridge sulfonates groups in a distorted tetrahedral manner (Ag2−O = 2.359(3), 2.410(3) Å). Owing to the ability of sulfonate groups to ligate
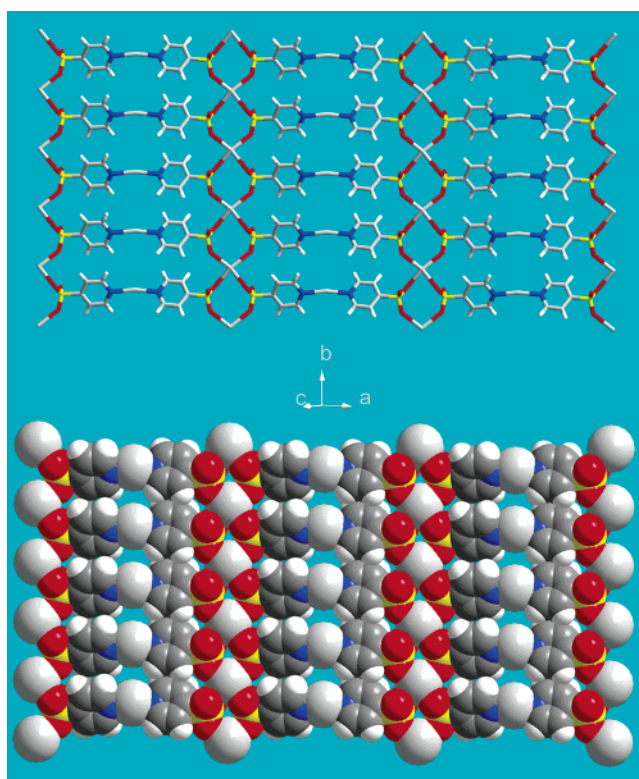

Figure 1. Stick (top) and space-filling representations of a single layer of **1** showing the two distinct Ag centers as well as the continuous layer structure.
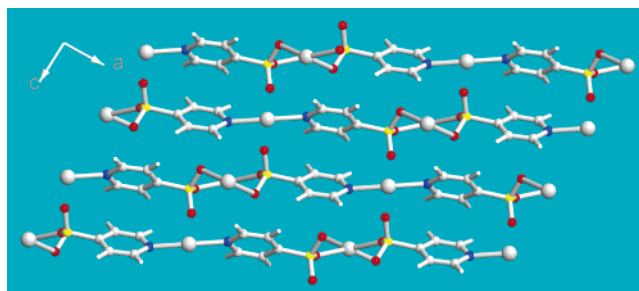

Figure 2. Ball-and-stick view of **1** looking in the plane of the layers showing the relative orientations of four adjacent sheets.

efficiently in two dimensions, the layers have a continuous rather than open grid structure. Adjacent [Ag(**L**)$_2$]$^-$ bricks are in close proximity but are not π-stacked within a layer. Pyridyl rings are separated along the b-direction by 5.410-(2) Å, paralleling the silver−silver distance. Adjacent layers are ordered by two sets of weaker interactions (Figure 2). The first is a very long Ag1−O3 interaction at 3.109(3) Å (sum of vdW radii for Ag−O = 3.52 Å). Second, longer edge-to-face π interactions (aryl−aryl distances = 3.477−

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(14) Compound **1** is only sparingly soluble in most solvents including MeOH. Crystal data for **1**: Ag$_2$C$_{10}$H$_8$O$_6$S$_2$, FW = 532.04 g mol^{-1}, colorless plates, monoclinic, space group C2 (No. 5), a = 15.089(3) Å, b = 5.4096(11) Å, c = 8.0336(16) Å, α = γ = 90.00°, β = 93.31-(3)°, V = 654.7(2) Å^3, Z = 2, D$_c$ = 2.699 Mg m^{-3}, R = 2.49%, R$_w$ = 5.45%, and GoF = 1.071 for 101 parameters using 1397 (F$_o$ > 2.0σ(F$_o$)) reflections. Flack parameter = −0.03. Mo Kα radiation (λ = 0.71073 Å), μ(Mo Kα) 3.342 mm^{-1}. The structure was collected on a Nonius Kappa CCD diffractometer at −100 °C. The structure was solved by direct methods and refined by full-matrix least squares, based on F^2, by using SHELXL-97.[20] Silver and sulfur atoms were located first and the remaining atoms were found by difference Fourier maps. All non-hydrogen atoms were refined anisotropically.
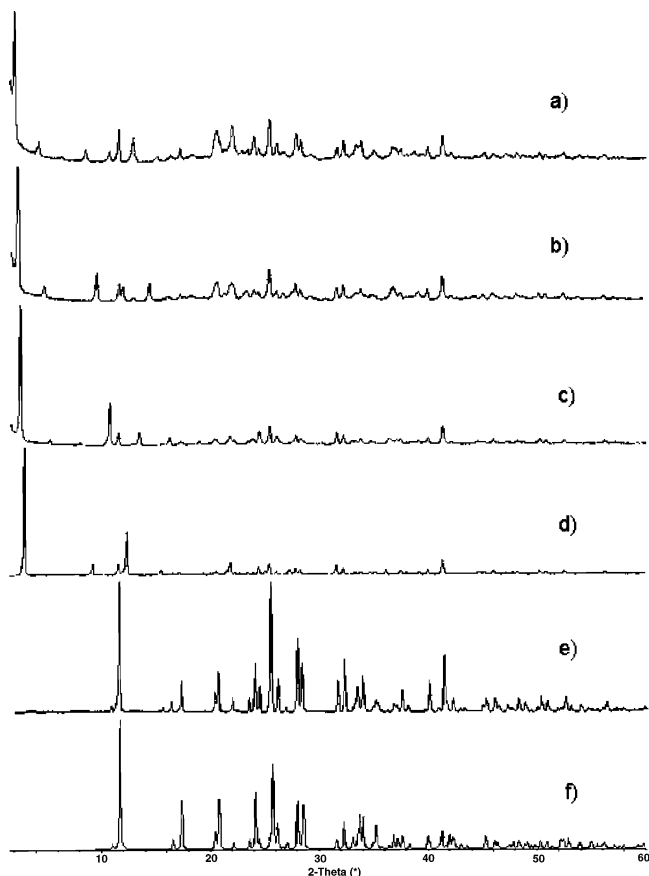
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Figure 3. PXRD patterns for (a) **1**·tetradecylamine; (b) **1**·dodecylamine; (c) **1**·decylamine; (d) **1**·octylamine; (e) bulk **1**; and (f) **1** simulated from single-crystal data.

3.583(4) Å) exist to one side only between each pyridyl ring and a pyridyl ring in a different layer.

In a 1:1 ratio, silver(I) and a simple organosulfonate will form a true hybrid inorganic−organic solid.[3a−c] *In 1, the more strongly ligating pyridine unit leads to the initial formation of $[Ag(L)_2]^-$ bricks, which then enforces a charge mismatch between the remaining silver(I) centers and the SO_3^- units.* The result is the observed 1:2 Ag/SO_3^- linear aggregate rather than layers. We have observed a similar directional role of the pyridine, that is, away from layers, in the 3-D solid, Ag(3-pyridinesulfonate).[10b]

The stability of host **1** was examined by thermal analysis. DSC showed that **1** was stable to 273 °C at which point an endothermic transition occurred. TGA showed the sample to be stable to mass loss until 330 °C at which point a mass loss of 42% was observed corresponding to loss of **L** and decomposition. This considerable thermal stability prompted an examination of both the chemical stability and potential functionality of **1** by examining its intercalation behavior.

A 1:1 amine/**L** ratio of the primary amines octyl, decyl, dodecyl, and tetradecylamine were individually dissolved in ether and added to a suspension of **1** also in ether. Upon treatment with the amines, crystalline **1** becomes a waxy material but is still air and light stable. Figure 3 shows the PXRD of these complexes along with host **1**. The PXRD patterns of all complexes were characteristic of layered solids with the most intense reflections arising from an equally

spaced Bragg family of planes {0 0 n}. The value for the lowest angle (0 0 1) Bragg reflection for each of the intercalates increases linearly, from 27.88(2) Å for **1**·octylamine to 39.22(2) Å for **1**·tetradecylamine, in direct proportion to the number of carbon atoms in the amine. The magnitudes of these values are too large for formation of an interdigitated structure, where the alkyl chains of amines interacting with adjacent layers interlock like the fingers of folded hands; thus, a bilayer arrangement of the guests is required. The slope of a plot of length of amine molecule (or alternatively simply number of C atoms in the amine) versus the increase in d spacing shows that the intercalated amines are tilted at an angle of 49° from the perpendicular.[15] Preliminary solid state ^{109}Ag NMR data confirm that the layer structure is retained in the intercalates as neither of the resonances for the two types of Ag centers are significantly perturbed relative to those of the host network.[16] Interestingly, this indicates that the amines are not coordinated strongly to either Ag center. Upon heating, the amines can be removed to regenerate the host in its nascent form as confirmed by PXRD.

To determine whether the intercalation was selective, the sorption experiments were repeated using guests containing other functional groups. In the presence of straight chain alkanes, nitriles, alcohols, and aldehydes, as well as benzene, toluene, and mesitylene, no guest uptake was observed. PXRD analysis showed no change in the host diffraction patterns. Selectivity was also examined by studying the series (n-Bu)NH$_2$, (n-Bu)$_2$NH, and (n-Bu)$_3$N in competitive experiments with one another.[17] Compound **1** was treated with an equimolar mixture (1 eq/Ag center) of all three amines and after 15, 30, 60, and 180 min, PXRD of solids as well as gas chromatographic analysis of the liquid in contact with **1** were performed. From the GC analysis, the absorbed amounts of the primary amine were 76, 89, 92, and 96% of the total present, respectively. Notably, in the presence of (n-Bu)-NH$_2$, within a 1% error, *neither (n-Bu)$_2$NH nor (n-Bu)$_3$N were intercalated at all*, illustrating that the network is highly selective for the primary amine. In the experiment involving only the secondary and tertiary amines, the secondary amine was preferentially absorbed with uptakes of 31, 37, 55, and 70% after 15, 30, 60, and 180 min, respectively. Thus, in the absence of the primary amine, intercalation of the secondary amine does take place but at a significantly slower rate. Even in the absence of primary and secondary amines, the tertiary amine is not absorbed by **1**. Given that the intercalation of the primary amine would be favored based on its coordinating/H-bonding ability, sterics, and the fact

(15) The plot indicates an increase in d of ∼0.97 Å for each C atom in the chain. A perpendicularly oriented all-trans amine bilayer would show an increase of ∼1.27 Å per C atom. The observed increase is consistent with a tilt of 49° from the perpendicular.

(16) Initial results indicate two distinct resonances for the pyridine and SO$_3$ ligated Ag centers. Complete ^{109}Ag SS NMR data on a range of intercalates will be reported in a full paper to follow.

(17) Equimolar amounts (2 mmol) of (n-Bu)NH$_2$, (n-Bu)$_2$NH, and (n-Bu)$_3$N were combined with tetradecane (5 mL). This mixture was then added to the solid host and stirred at room temperature. Aliquots (20 μL) were removed from the mixture at various time intervals (0, 15, 30, 60, and 180 min) and subjected to GC−MS analysis. This procedure was then repeated with only the secondary and tertiary amine present.

that the monoamines would pack more efficiently in the interlayer, this complete selectivity is perhaps not that surprising.

Amine or alcohol intercalation has been observed for a number of metal phosphonates.[8] Interestingly, selectivity for primary amines has also been observed.[8g] With regard to metal sulfonates, we have observed topotactic intercalation of alcohols in Ag triflate.[18] In these structures, the inorganic backbone has the prototypical pattern of metal centers bridged by oxo-anions with pendant organic moieties. Compound **1** is unusual in that the organic unit forms part of the layer itself. Significantly, this reduces the density of the interactions used to stitch the layers together, yet intercalation phenomena are still observed. A facile means of regulating the organic nature of the layer would be to vary the length of the organic linker between the pyridyl and sulfonate moieties. Thus, whereas in a typical hybrid inorganic−organic solid the inorganic skeleton itself has a regular, and not easily altered structure, the backbone in this solid can be modified. This is of note as exfoliated layered solids can be employed for reinforcing engineered polymers where an issue is the surface compatibility of the exfoliated solid with the organic polymer being reinforced.[19] Extending the core in **1** would provide a means of tuning the organic nature of this layered material, a much-stated fundamental benefit to a coordination solid approach.

In the present work, we have reported a new type of continuous layer coordination solid which selectively intercalates primary > secondary ≫ tertiary amines as well as showing selectivity over other classes of organic guests. The layered host is of note for three reasons. In contrast to hybrid inorganic−organic solids, the organic moieties are incorporated in, rather than pendant to, the layers. In contrast to most metal−organic structures, the layers are continuous. Finally, despite having a lower density of linking interactions in a layer, which should correlate to lower stability, **1** is both chemically and thermally quite stable as illustrated by the observed intercalation phenomena.

Supporting Information Available: Crystallographic information file (CIF) for **1**. Preparations and spectral characterization of **L** and **1**, and chromatographic data for selective inclusion experiments (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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