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Structure−Spectroscopy Correlations in Silver Thiolates: Application to the Structure of Silver 1,5-Pentanedithiolate

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A variety of spectroscopic methods have been used to deduce the solid-state structure of $Ag_2[S(CH_2)_5S]$ (**1**), the yellow compound formed by mixing of Ag^+ and 1,5-pentanedithiol. Solid-state reflectance UV−vis, X-ray diffraction, cross-polarization magic angle spinning (CPMAS) ^{13}C NMR, and CPMAS ^{109}Ag NMR spectra of **1** were compared to corresponding spectra for two crystallographically-characterized homoleptic Ag thiolates, the cluster $Ag_5\{\mu^2\text{-}S(CH_2)_3N(CH_3)_2\}_3\{\mu^2\text{-}S(CH_2)_3NH(CH_3)_2\}_3(ClO_4)_2$ (**2**) and the infinite strand $AgSC(CH_2CH_3)_2CH_3$ (**3**). Two limiting geometries for **1** are considered: a linear polymer and a layered geometry similar to that adopted by neutral Ag thiolates with primary, unbranched alkane chains. All spectroscopic data are consistent with the latter structure. Information about alkane chain orientation and Ag−S vibrational modes in **1** was obtained by comparison of low-wavenumber Raman and diffuse reflectance infrared Fourier transform (DRIFT) spectra with those for all-trans $AgS(CH_2)_3CH_3$ (**T**) and the C(1)−C(2) gauche isomer (**G**). The spectra show that the majority of alkane chains in **1** adopt a fully extended, all-trans geometry, but that gauche conformers are clearly present. These experiments demonstrate that sensitive structure elucidation can be achieved by combination of solid-state spectroscopic methods, when appropriate standards are available. Although isostructural layered, neutral compounds of the form AgSR exhibit liquid crystalline behavior upon melting, **1** does not, a consequence of covalent attachment between layers.

Introduction

Mixing of solutions containing Ag^+ and primary, unbranched organic thiolates $[CH_3(CH_2)_nSH]$ typically leads rapidly to insoluble precipitates. The resulting solids exhibit an infinite-sheet, two-dimensional (2-D), nonmolecular layered structure[1,2] (Scheme 1) that provides a marked contrast to the crystalline materials that have been obtained with primary 1,2-dithiolates, secondary thiolates, or tertiary thiolates.[3,4]

Several attributes of these layered AgSR species (R = primary alkyl) are of interest. First, they exhibit liquid crystalline behavior upon melting[5] and have been described as "covalent soaps".[2] Two structural motifs are thought to mediate mesophase formation upon melting: (i) the ability of thiolates to switch from μ^3 (triply bridging) to μ^2 (doubly bridging) coordination, with a concomitant change in Ag coordination from trigonal (3-coordinate) to digonal (2-coordinate); and (ii) disruption of interlayer CH_3−CH_3 contacts to form stacked-disk micellar structures.[2] Support for this mechanism of mesophase formation is provided by studies showing that, with bulky R groups, dissociation of infinite AgSR solids in solution leads to cyclic $(AgSR)_n$ species.[6,7]

The structure in Scheme 1 is also of interest as a 3-D analog of 2-D organothiol self-assembled monolayers (SAMs)[8] on Ag.[9] Spectroscopic studies of AgSR compounds allow the bonding in the hexagonal Ag−S lattice to be probed, and the structural consequences of relaxed chain occupancy—the structure in Scheme 1 has a per-layer alkane chain density one-half that of

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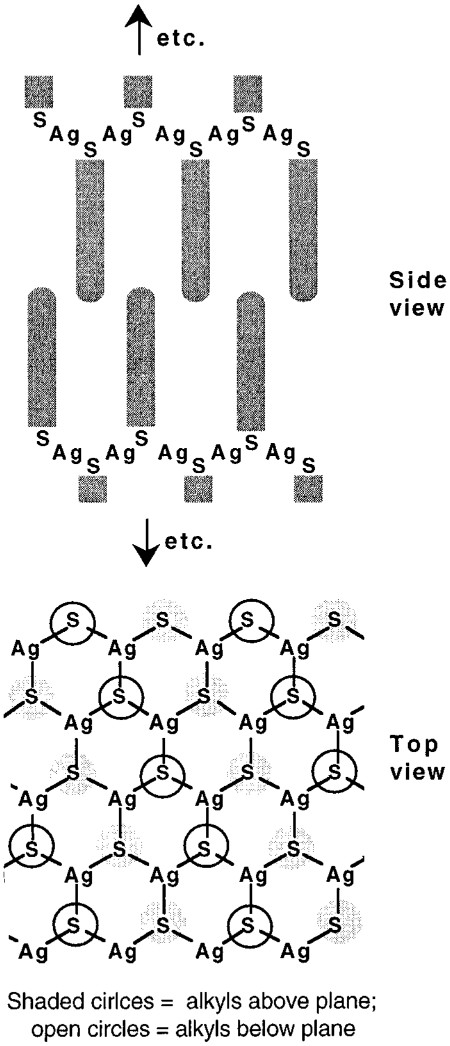
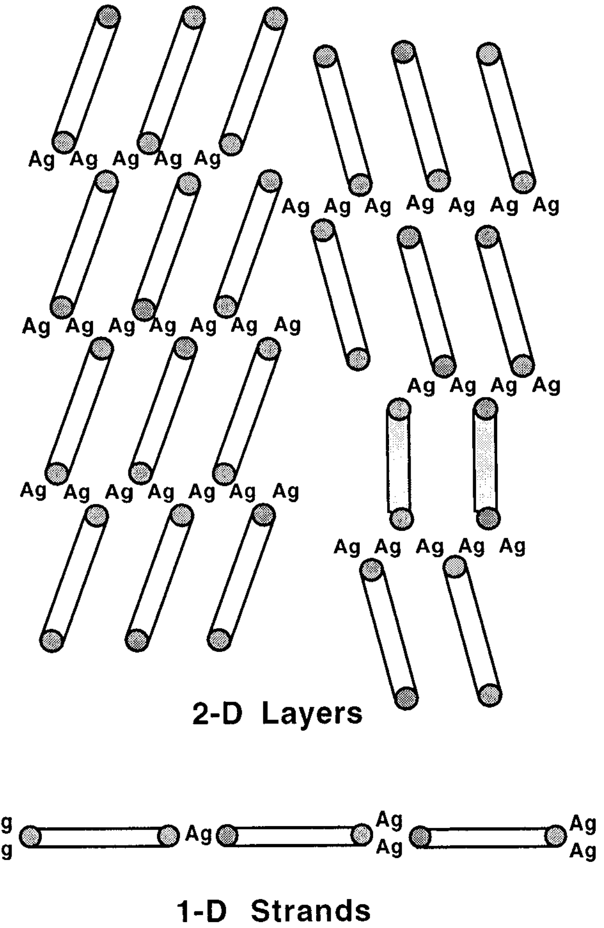
Scheme 1. Layered Structure of $AgS(CH_2)_nCH_3$



Scheme 2. Possible Structures for **1**



a close-packed SAM—to be understood.[10] Such spectroscopic studies also shed light on the structures of metalloproteins and metallopeptides that bind Ag^+ via complexation to deprotonated cysteine side chains ($-CH_2S^-$).[11]

We recently showed that cross-polarization magic angle spinning (CPMAS) ^{109}Ag NMR is a very sensitive probe of Ag^+ coordination environments in homoleptic thiolate complexes.[12] In that work, ^{109}Ag NMR spectra of structurally-characterized complexes provided a database that was used to elucidate details of Ag^+ coordination in noncrystalline materials. We are in the process of extending this concept to several other spectroscopic methods for solids (UV−vis, X-ray diffraction, CPMAS ^{13}C NMR, Raman, and diffuse reflectance infrared Fourier transform (DRIFT)[13] spectroscopy) in order to establish a comprehensive structure−spectroscopy database. Our motivation for this work is to be able to determine structural information on Ag^+-containing solids from which crystals suitable for X-ray crystallography cannot be obtained.

We describe herein the application of this approach to $Ag_2[S(CH_2)_5S]$ (**1**), the yellow compound formed by mixing of Ag^+ and 1,5-pentanedithiol. In principle, **1** could adopt a layered structure analogous to that depicted in Scheme 1 for AgSR (R = primary alkyl), but without methyl group van der Waals interactions and interdigitation (Scheme 2, top). An alternative structure involves linear bridging to yield amorphous polymer strands (Scheme 2, bottom), a motif previously observed in reactions of Hg^{2+} with dithiols.[14]

Structure determination of **1** was facilitated by spectroscopic comparison to three compounds: $Ag_5\{\mu^2\text{-}S(CH_2)_3N(CH_3)_2\}_3\{\mu^2\text{-}S(CH_2)_3NH(CH_3)_2\}_3(ClO_4)_2$ (**2**),[15] $AgSC(CH_2CH_3)_2CH_3$ (**3**),[7] and $AgS(CH_2)_3CH_3$ [both the fully extended, all-trans species (**T**) and the gauche C(1)−C(2) conformational isomer (**G**)].[1,10] For **2** and **3**, crystal structures are known. **2** consists of an Ag_5S_6 trigonal prismatic core with both two- and three-coordinate Ag−S environments (Scheme 3).[15] **3** is a one-dimensionally nonmolecular solid, consisting of interwoven, non-bonded pairs of $(Ag-SR)_\infty$ strands, with linear, 2-coordinate Ag−S bonds.[7]

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(10) X-ray diffraction, ^{13}C NMR, ^{109}Ag NMR, diffuse reflectance UV−vis, and Raman data for **T** and **G** can be found in the following: Fijolek, H. G.; Grohal, J. R.; Sample, J. L.; Natan, M. J. *Inorg. Chem.* **1997**, *36*, 622.

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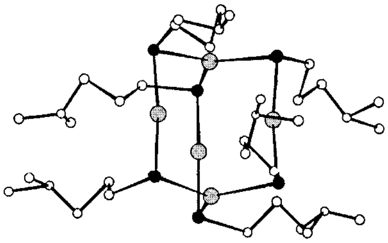
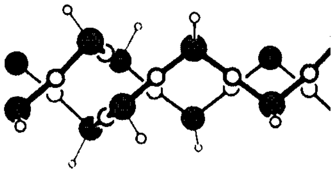
Scheme 3. Structurally-Characterized Silver Thiolates



2: Gray circles = Ag, dark circles = S, open circles = C



3: Large open circles = Ag, small open circles = C, dark circles = S

Uv-vis, ^{109}Ag NMR, X-ray diffraction, and ^{13}C NMR studies of **1**−**3** indicate that **1** adopts a layered structure like that shown in Scheme 1 and the top of Scheme 2. However, it does not form liquid crystals upon melting. Raman and DRIFT spectra of **1**, **T**, and **G** show that most of the alkane chains in **1** exist in a trans configuration, but gauche C(1)−C(2) conformers are also present. Together, these data show how a combination of spectroscopic measurements can serve as a reasonably effective structural determinant when crystallographic data are unavailable.

Experimental Section

Materials. $AgNO_3$ (99+%, Aldrich), 1,5-pentanedithiol (Aldrich), acetone (Fisher Scientific), and CH_3OH (Fisher Scientific) were used as received. H_2O (18 MΩ) was distilled and deionized on a Barnstead Nanopure Analytical water filtration system.

Synthesis. $Ag_2[S(CH_2)_5S]$ (1). This synthesis was carried out in Al foil-wrapped flasks to protect the reactants and products from light exposure. A solution of $AgNO_3$ (2.06 g) in 20 mL of H_2O was added dropwise to 1.70 g of $HS(CH_2)_5SH$ in 20 mL of acetone. The resulting yellow solid was filtered, washed with cold H_2O, and dried overnight under vacuum. Melting point = 108 °C dec. Elemental analysis (Schwarzkopf Microanalytical Laboratory) for $C_5H_{10}S_2Ag_2$: C, 17.16; H, 2.88; S, 18.32; Ag, 61.64. Found: C, 18.01; H, 2.79; S, 19.24; Ag, 57.35; N, 0.37. Syntheses of **2**,[15] **3**,[7] **T**,[10] and **G**[10] are described elsewhere.

Instrumentation. Diffuse reflectance electronic spectra were obtained with a Perkin-Elmer Lambda 9 double-beam, double-monochromator UV/visible/infrared spectrophotometer using an integrating sphere with $BaSO_4$ as the reference. Far-IR diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained with a Nicolet Magna-IR System 750 with a deuterated triglycine sulfide−polyethylene (DTGS−PE) detector and ground polyethylene used as background. For controlled experimental conditions, a special beam collector with an environmental chamber for temperature control (Spectra Tech Inc.) was used. The instrument was purged with N_2 gas from a liquid N_2 tank at a flow rate of 450 mL/min. Raman spectra were obtained using the 568.2 nm line of a Spectra Physics Model 164 laser equipped with an Excitek mixed-gas (Ar^+/Kr^+) plasma tube. Detection was carried out using a Spex 1877 triple monochromator equipped with a 1200 grooves/mm spectrograph grating, a 600 grooves/mm filter stage grating, and a UV-coated, liquid-N_2-cooled CCD detector. Solid-state ^{109}Ag and ^{13}C spectra were acquired at 294 K on a Chemagnetics CMX-300 spectrometer operating in the quadrature mode at 13.852 MHz for ^{109}Ag, 74.78 MHz for ^{13}C, and 297.37 MHz for ^{1}H. A Doty Scientific multinuclear double-tuned 10 mm Supersonic probe was used for ^{109}Ag experiments, and a Chemagnetics multinuclear double-tuned 7.5 mm Pencil probe was used for ^{13}C experiments. $AgOOCCH_3$ was used as a secondary standard reference (382.7, 401.2 ppm relative to $AgNO_3$)[12] for ^{109}Ag NMR experiments, and hexamethylbenzene [132.21 ppm relative to $Si(CH_3)_4$] was used as the reference for ^{13}C NMR experiments. X-ray diffraction data were obtained on a Philips X'Pert powder diffractometer in steps of 0.02° 2θ using graphite-monochromated Cu Kα radiation. Melting points were measured using a Mel-Temp II (Laboratory Devices). Liquid crystal properties were investigated using a Nikon Optihot-Polarizing microscope fitted with a Mettler FP82 hot stage, the latter being controlled by a Mettler FP80 central processor.

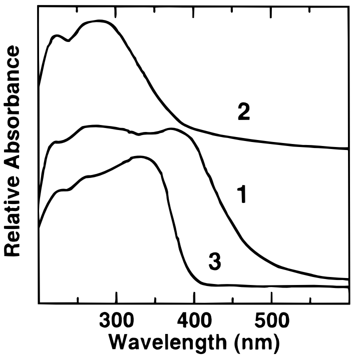


Figure 1. Solid-state diffuse reflectance spectra of compounds **1**−**3**. For clarity, spectra are offset vertically.

Results

It is has been stated that 3-coordinate Ag thiolates are yellow and 2-coordinate complexes are white.[3,4] The solid-state diffuse reflectance spectrum of the yellow-brown compound **2**, which has both 2-coordinate and 3-coordinate Ag^+ ions, exhibits an intense band at 280 nm and an extremely long tail that persists to almost 500 nm (Figure 1). The latter feature is responsible for the yellow-brown color and is very likely a S → Ag ligand to metal charge transfer (LMCT) band, by analogy to other d^{10} metal thiolate complexes.[1] The 2-coordinate compound **3** also exhibits an intense ultraviolet band at 340 nm but no tail in the visible—notice the very sharp drop at 400 nm—and accordingly is white.

Compound **1** is bright yellow in color, and the solid-state diffuse reflectance spectrum exhibits an intense feature at 400 nm that tails substantially into the visible region of the electromagnetic spectrum. This strongly suggests the presence of Ag^+ ions in a 3-coordinate environment. On the basis of photophysical studies of AgSR compounds (R = primary alkyl), the spectral feature in the visible derives from a S → Ag LMCT band.[17] Interestingly, the LMCT state is emissive; excitation of solid **3** at 426 nm leads to a feature in the emission spectrum with a maximum at 698 nm (data not shown).[17]

X-ray powder diffraction data for compounds **1**−**3** is shown in Figure 2. Powder patterns of both **2** and **3** clearly indicate their crystalline character, as previously observed in single-crystal studies of these compounds.[7,15] In principle, compound **1** could be related to a series of alkanethiols that have previously been shown to be microcrystalline in nature, with layered structures;[1] in this case, the alkanedithiol would replace two alkanemonothiols in Scheme 1. In fact, **1** does diffract X-rays, suggesting a layered structure. However, the paucity of lines and the roughly exponential decrease in intensity for the first few lines both suggest poor registry between layers. An interlayer spacing of ≈10.6 Å can be estimated using the Bragg

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(17) Fijolek, H. G.; Natan, M. J. Unpublished observations.

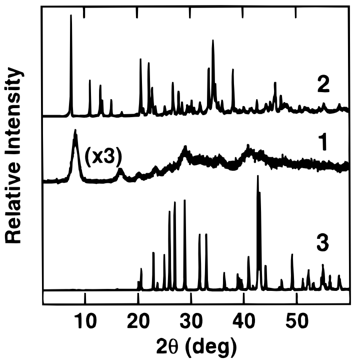

Figure 2. X-ray powder diffraction patterns of **1**−**3**. For clarity, spectra are offset vertically.

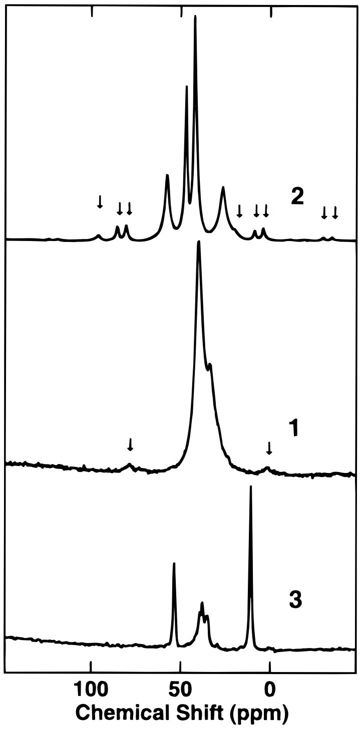

Figure 3. ^{13}C CPMAS NMR spectra of **1**−**3**. Conditions: pulse delay, 4 s; contact time, 5 ms; ring-down delay, 20 μs; spinning rate, 3 kHz. Top: 6500 transients. Middle: 6768 transients. Bottom: 8224 transients. Spinning side bands are marked with arrows.

formula, but the broadness of the peaks indicates disorder, resulting from variations in layer spacing.

^{13}C NMR spectra provide information, from the number and width of peaks, about the alkane chain chemical environment, and thereby can corroborate X-ray-based information about order/disorder. In **2**, which has in principle 10 different C environments (five each for $CH_2CH_2CH_2N(CH_3)_2$ and $[CH_2CH_2CH_2NH(CH_3)_2]^+$) four distinct peaks are observed in the 25−75 ppm region, a result of C_3 and C_2 symmetry axes. The ^{13}C CPMAS NMR spectrum of **2** also reveals aspects of alkane chain dynamics in the solid state: spinning side bands (SSBs) of the isotropic peaks (denoted by arrows, Figure 3) are indicative of an unusual rigidity in the alkane chains. Such side bands are normally observed in alkanes only when rotation about the C−C bond is inhibited.[18] The cagelike crystal structure of compound **2**, in which adjacent chains can undergo hydrogen bonding through the −N− and −NH− moieties, results in hindered alkane chain rotation.

The ^{13}C NMR spectrum of **1** consists of large and small overlapping peaks around 40 ppm, indicating similar chemical environments for each $-CH_2-$ group. Despite the disorder observed in the X-ray powder pattern of **1**, the presence of small SSBs in the ^{13}C NMR spectrum implies that the $-(CH_2)_5-$ chains are unable to undergo molecular motion in the solid. Interestingly, such rigidity is not observed with analogous compounds based on linear monothiols,[10] suggesting that the rigidity derives in part from tethering both ends of the alkane to planes of Ag^+. In contrast, the zigzag Ag−S structure of compound **3** permits free rotation of the $-C(CH_3)(CH_2CH_3)_2$ side chains, as evidenced by the lack of SSBs.

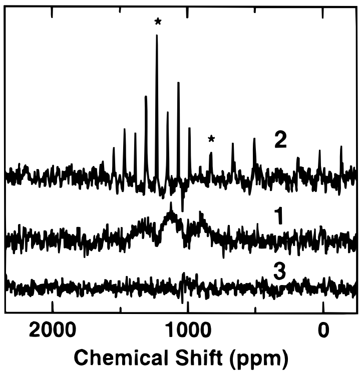

Figure 4. ^{109}Ag CPMAS NMR spectra of **1**−**3**. Conditions: pulse delay, 3.5 s; contact time, 15 ms; ring-down delay, 80 μs. Top: spinning rate, 2.2 kHz; 6524 transients. Middle: spinning rate, 4.0 kHz; 8192 transients. Bottom: spinning rate, 4.0 kHz; 4096 transients. Isotropic peaks of **2** are starred.

The ^{109}Ag NMR spectra of **1**−**3** (Figure 4) provide an intriguing contrast to the powder patterns of Figure 2. It has previously been observed that ^{109}Ag NMR is extremely sensitive to differences in Ag environment; small differences in bond lengths and angles result in very different isotropic shifts.[12,19] Compounds that have a one-dimensional nonmolecular structure typically have such a wide range of slightly different Ag environments that signals from the Ag cannot be seen above the background noise.[12] **3** meets this criterion, and its ^{109}Ag NMR spectrum is featureless. Compound **2**, in contrast, possesses two distinct, very well-defined environments in a rigid crystal structure, giving rise to two corresponding isotropic peaks at 1228 and 826 ppm. The ^{109}Ag NMR spectrum of **1** exhibits an envelope of isotropic peaks, with partially overlapping spinning side bands that cluster into three humps. These data illustrate that **1** is somewhere between compounds **2** and **3** with respect to the variety of Ag environments present. This shows that, although the powder pattern of **1** indicates that this compound is somewhat disordered, the Ag environments are not as poorly defined as in crystalline **3**. Note that the chemical shift envelope for **1** falls largely between the two isotropic peaks for **2**, which correspond to 2-coordinate and 3-coordinate environments. As a result, it is not possible to definitively assign a coordination number to the Ag^+ ions in **1** from the ^{109}Ag NMR data alone.

Information about the orientation of the alkane chains is available through vibrational spectroscopy. Of particular interest is whether the C(1)−C(2) bond exhibits an all-trans configuration [i.e., S anti to C(3)] or a gauche conformation [i.e., S gauche to C(3)]. Both of these orientations are known for alkanethiolates adsorbed on Ag or Au surfaces.[8,9] Moreover,

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(18) The spinning side bands give a measure of the chemical shift anisotropy, which for **1** and **3** at room temperature is equivalent to that of most flexible organic compounds at 77 K or below. For example, see: Duncan, T. M. *A Compilation of Chemical Shift Anisotropies*; Farragut Press: Madison, WI, 1990. Fyfe, C. A. *Solid State NMR for Chemists*; CRC Press: Guelph, Ontario, 1983; Chapter 5.

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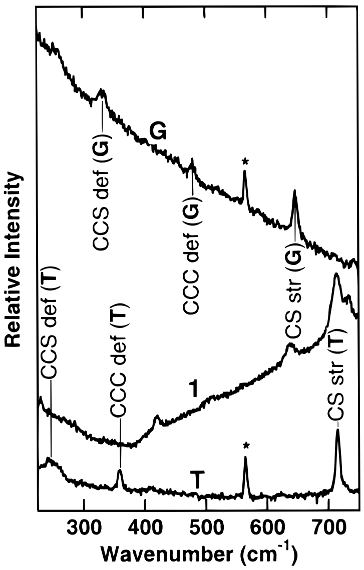

Figure 5. Raman spectra of **G**, **1**, and **T**. Conditions: 568.2 nm laser line, 30 mW at sample, 10 s integration time. For clarity, spectra are offset vertically.

the layered compound $AgS(CH_2)_3CH_3$ can be isolated in three different forms, an all-trans species (**T**), an all-gauche species (**G**), and a mixed phase (**G/T**).[10]

The low-wavenumber Raman spectra of **1**, **G**, and **T** are shown in Figure 5. Two of the three bands in the spectrum for **1** can be assigned by comparison to known bands in **G** and **T**:[10] the strong band at 714 cm^{-1} is the C−S stretch for the trans species, while the weaker band at 640 cm^{-1} is the corresponding stretch for the C(1)−C(2) gauche isomer. These bands have previously been assigned for alkanethiols in solution[20] and adsorbed and Ag surfaces.[21,22] The presence of both gauche and trans C(1)−C(2) isomers for **1** is reminiscent of **G/T**, which also exhibits both alkane chain orientations.[10] The weak band at 421 cm^{-1} can be assigned as a CCC deformation, based on arguments detailed below. Finally, we are not able to definitively assign the band on the high-energy side of the trans ν(C−S) mode for **1** (at 735 cm^{-1}). However, on the basis of spectral comparison to known compounds, it is neither a S−Ag stretch[17] nor a C−S mode,[20−22] and thus it is probably a C−C backbone mode.

The corresponding low-wavenumber infrared vibrational data have been acquired using DRIFT, a method that has seen little application in transition metal chemistry.[23] DRIFT spectra for **G**, **T**, and **1** are shown in Figure 6. For the trans and gauche isomers of $AgS(CH_2)_3CH_3$, band identification is facilitated by comparison to published assignments. Thus, 410 and 369 cm^{-1} bands in **T** correspond to CCC deformations in a trans C(1)−C(2) isomer. The corresponding vibration in the **G** isomer at 478 cm^{-1} has been identified in neat butanethiol and for butanethiolate adsorbed to colloidal Ag.[22a] In **1**, the sharp feature observed at 424 cm^{-1} is most reasonably assigned to a trans CCC deformation, on the basis of its proximity to the 410 cm^{-1} band of **T**. Note that thiolate coordination to two Ag^+ ions could easily shift this vibration by ≥10 cm^{-1}, a phenomenon that has been observed for the C−S stretch.[22a]

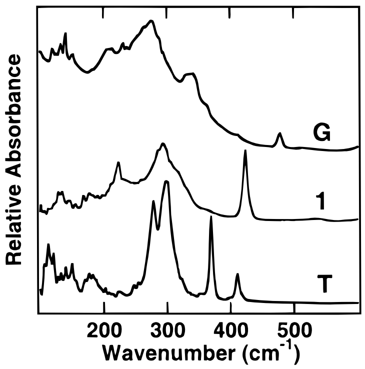

Figure 6. DRIFT spectra of compounds **G**, **1**, and **T**. For clarity, spectra are offset vertically.

Band assignment for peaks ≤300 cm^{-1} is problematic, in part due to the paucity of low-wavenumber infrared data on alkanethiolates. In **T**, the intense bands at 278 and 298 cm^{-1} could be assigned either to Ag−S vibrations or to other internal butanethiolate modes, possibly CCS deformations. Similarly, **1** has a broad peak at 293 cm^{-1}, which may be a convolution of the two peaks seen in **T**. For neat (liquid) propanethiol, a Raman band at 290 cm^{-1} was assigned as a CCS bend for both trans and gauche isomers.[24] In 1,2-ethanedithiol, the CCS deformation of the gauche isomer was assigned to a pair of bands at 267 and 403 cm^{-1}, while the trans isomer exhibited a vibration at 299 cm^{-1}.[25] The Raman spectrum of liquid butanethiol has bands at 248 and 300 cm^{-1} that are assigned as CCS deformations; the absence of the 300 cm^{-1} band in the solid state led Nandy and Mukherjee to assign it to the gauche isomer.[26] Since **T** is known to have a trans orientation, the bands in the 290−300 cm^{-1} region of **T** and **1** cannot therefore be CCS deformations.

An analysis by Bowmaker and Tan of low-frequency vibrational data of several Cu and Ag alkane- and arenemonothiolate complexes has allowed assignment of metal−sulfur stretching bands. IR data acquired at ca. 120 K for $AgSBu^t$ (Bu^t = 2-methylpropane-2-thiolate) reveal strong bands at 348 and 240 cm^{-1}; the presence of a 348 cm^{-1} band in $CuSBu^t$ suggested that it was an internal vibration of the ligand, and the band at 240 cm^{-1} was assigned to the Ag−S stretch.[27] However, we have observed a frequency dependence of the Ag−S stretch on coordination environment,[17] just as has been previously described for homoleptic Hg^{2+}−thiolate complexes.[16] Indeed, structurally-characterized Hg−S compounds exhibit Hg−S IR stretches that range from 165 to nearly 400 cm^{-1}.[16] Thus, the 278 and 298 cm^{-1} bands of **T** and the 293 cm^{-1} of **3** are tentatively assigned to Ag−S vibrations.

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Support for this assignment comes from IR studies of Au thiolate complexes. The force constant for AuCl (S and Cl have almost identical masses) exceeds slightly that for AgCl.[28] This tends to raise the frequency of Au−S vibrations relative to Ag−S vibrations. On the other hand, the increased mass of Au leads to lower frequencies. The net effect is that Au−S and Ag−S vibrations are more or less isoenergetic. With the assignment of a 244 $\mathrm{cm^{-1}}$ infrared band in $[\mathrm{Au(SBu^t)_2}]^-$ to an Au−S stretch,[30] assignment of bands 40−50 $\mathrm{cm^{-1}}$ higher in energy to Ag−S vibrations is reasonable.

Examination of **1** under a polarizing microscope fitted with a hot stage indicated no liquid crystal behavior. Note that the absence of a stable liquid phase does not preclude observation of liquid crystal behavior: **G** melts with decomposition at 185 °C,[10] but exhibits liquid crystalline properties (like **T**)[2] well before melting.

Discussion

As a prelude to considering spectroscopic data on **1**, it is instructive to consider similarities and differences between the layered structure and linear strands depicted in Scheme 2. Mixing $\mathrm{Ag^+}$ and 1,5-pentanedithiolate could easily lead to polymeric species (1-D strands) with end-on monodentate S coordination. Indeed, **3** is such a polymer, with intertwining strands (Scheme 3, bottom)! Note that the presence of weak, distant bonds between $\mathrm{S^-}$ and $\mathrm{Ag^+}$ atoms on adjoining strands increases the effective coordination number for $\mathrm{Ag^+}$ and also helps satisfy the $18\mathrm{e^-}$ rule. In theory, strand alignment could be ordered enough (as shown in Scheme 2) to diffract X-rays. If so, the observed interlayer spacing would be 13 Å, the sum of the length of the 1,5-pentanedithiolate ligand (7.9 Å from S nucleus to S nucleus, assuming an all-trans geometry) and twice the sum of a Ag−S bond (2.55 Å). If the alkane chain assumed had one or more gauche kinks, this value would be lower.

Ag−S bonding is fundamentally different in the layered structure, as all end-on bonding is eliminated: each $\mathrm{S^-}$ and $\mathrm{Ag^+}$ bridges to three of the opposite atoms (Scheme 1, top view). Consequently, each $\mathrm{Ag^+}$ is 3-coordinate, perhaps leading to the expectation that all such layered species are colored. However, this is not correct: distortions of the hexagonal lattice can lead to T-shaped geometries with one long and two short Ag−S bonds. **T**, which is white, exhibits such a geometry.[1,10]

Neither the hexagonal nor the distorted hexagonal lattice is required to be planar; in fact, X-ray data on AgSR compounds of varying alkyl chain lengths[1,2,10] indicate that the Ag−S slab is ≥1 Å thick. As result, calculation of the interlayer thickness in layered structures actually depends on four parameters: alkane chain length, alkane chain conformation, alkane chain tilt angle, and Ag−S slab thickness. It is also important to note that the presence of bridging S atoms requires that the Ag−S bond not be perpendicular to the $\mathrm{Ag^+}$ planes. Even in the absence of chain tilting or gauche kinks, this leads to reduced interlayer spacing relative to that expected for ordered 1-D strands.

Both the 1-D strand and 2-D layers in Scheme 2 are depicted with $\mathrm{Ag^+}$ vacancies. This is necessitated by the results of elemental analysis, which repeatedly yield a S:Ag ratio slightly greater than 1 (1.05−1.1). We and others have observed a similar phenomenon with neutral Ag thiolates using $\mathrm{CH_3(CH_2)_3SH}$, $\mathrm{HS(CH_2)_4SH}$, and $\mathrm{HS(CH_2)_6SH}$.[10,17,30] In the case of dithiols, this is easily explained by occasional reaction of just one of the two functional groups with $\mathrm{Ag^+}$. This similarity notwithstanding, there are fundamental differences in both Ag coordination environment and interlayer spacing between 1-D and 2-D models for **1**.

The spectroscopic data in Figures 1−6 are all consistent with the layered model. X-ray diffraction data in Figure 2 indicates an interlayer spacing of 10.6 Å, a value that could be accommodated by the end-on bonding in the 1-D structure only through the presence of at least one gauche bond in the alkane chain. However, Raman and infrared data (Figures 5 and 6, respectively) indicate that an all-trans chain configuration is predominant. The 2-D structure for **1** is also supported by both ^{13}C and ^{109}Ag solid-state NMR data (Figures 3 and 4, respectively). In the case of ^{13}C, spinning side bands indicate a rigid alkane backbone structure, a finding inconsistent with a 1-D polymeric strand, which would have flexible alkyl groups. ^{109}Ag data indicate the presence of several relatively well-defined Ag environments, as opposed to the large number of disordered environments present in species like **3**. The intense yellow color of **1**, characteristic of 3-coordinate $\mathrm{Ag^+}$ thiolates, also favors a layered geometry.

However, compared to layered $\mathrm{Ag^+}$ compounds with thiolate or carboxylate ligands,[31] **1** is relatively disordered. The X-ray diffraction data are weak, the lines are broad, and the number of reflections is small. These findings can be explained by poor registry between layers, variations in layer spacings, and heavy-atom vacancies. The peak envelopes in the ^{109}Ag NMR spectrum indicate the presence of multiple well-ordered environments for $\mathrm{Ag^+}$, as opposed to two isotropic peaks in **2**, which has only two $\mathrm{Ag^+}$ environments.

1 also exhibits both all-trans and gauche environments at C(1)−C(2). To determine the absolute amounts of trans and gauche species present would require relative values of the polarizabilities of each vibration in this molecule. These are not currently known, but on the basis of studies of **T** and **G**,[32] they can be crudely estimated as being roughly equivalent. Thus, gauche C(1)−C(2) bonds represent a minor conformational component.[33] It is interesting to note that the intense yellow color of **G** is related either directly or indirectly to alkane chain conformation, because **T** is white. In contrast, **1**, like **T**, has trans alkane chains, but is yellow, like **G**.

The right side of the layered structure in Scheme 2 reflects the spectroscopically-detected disorder in **1**. Thus, the alkane chain orientation is switched, molecules with a different tilt angle [perhaps those exhibiting C(1)−C(2) gauche interactions] are shaded gray, $\mathrm{Ag^+}$ registry between layers is imperfect, and the interlayer spacing is not constant. Whether this disorder is intrinsic to a particular class of compounds (HSRSH), a result of synthetic protocol, or other factors is not presently known.

1 exhibits no liquid crystalline properties, in contrast to a series of monodentate AgSR compounds ($\mathrm{R = C_3{-}C_{18}}$).[2] Given the structural similarities between these compounds, it seems clear that a van der Waals interaction between layers (Scheme 1) is necessary to promote mesophase formation. However, a change in $\mathrm{Ag^+}$ coordination number is not needed, as we have previously shown that a change from μ^3-bridging to μ^2-bridging

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[32] **T** converts cleanly to **G** upon heating. By integrating the Raman intensities for the trans and gauche C(1)−C(2) vibrations as a function of temperature, it can be shown that the trans:gauche polarizability ratio is ≈1.3:1.[17]

[33] Note that, by symmetry, **1** has two C(1)−C(2) bonds; it is not possible to tell whether the gauche interactions appear individually or in pairs.

does not occur in **T** or **G**, both of which exhibit liquid crystal behavior. These findings lead to synthetic opportunities for new liquid crystalline materials, as end groups other than CH_3 in RSH are easily prepared. For example, $-OH$ or $-CO_2H$ groups should exhibit hydrogen bonding between layers, which might lead to interesting effects upon melting. Given the extreme insolubility of AgSR complexes based on primary unbranched alkyls, it may even be possible to prepare layered structures with charged groups like NH_3^+. Synthesis and characterization of a variety of AgSR species is currently in progress.

Summary

Using a combination of solid-state spectroscopic methods, **1** was determined to have a layered structure, albeit with significant disorder. The disorder is not associated with individual Ag^+ environments, since ^{109}Ag peaks were detected. ^{13}C NMR data indicated a rigid alkane chain; vibrational spectroscopy showed that the alkane chain conformation was mostly all-trans. The liquid crystal behavior of **T**, **G**, and related AgSR species derives from noncovalent interlayer interactions, since **1** does not exhibit liquid crystal behavior.

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