Inorg. Chem. **2002**, *41*, 287–292

Inorganic Chemistry

Article

Intercalation of Alcohols in Ag Sulfonates: Topotactic Behavior Despite Flexible Layers

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Received July 27, 2001

This article presents the inaugural intercalation study of a layered metal sulfonate network. Silver triflate forms intercalation complexes with straight chain primary alcohols from ethanol (C_2H_5OH) to eicosanol ($C_{20}H_{41}OH$). Single-crystal data for the EtOH adduct, **1**, are presented which show that the intercalation is coordinative to Ag. In contrast to many other layered hosts, no preheating of Ag triflate is required to liberate a coordination site for intercalation to take place, owing to the ability of the triflate ion to reorient. Crystal structure parameters for **1**: $C_4H_6F_6S_2O_7Ag_2$, $a = 5.345(7)$ Å, $b = 11.310(2)$ Å, $c = 12.004(2)$ Å, $\alpha = 116.87(1)^\circ$, $\beta = 90.46(1)^\circ$, $\gamma = 99.59(1)^\circ$, triclinic, space group $P\bar{1}$, $Z = 2$. Intercalate **1** presents the triflate ion in an unprecedented μ^5-coordination mode. PXRD data on the family of complexes show that the intercalation is topotactic, as verified by the linear increase in *d*-spacing and calculated *c*-axis lengths for the intercalates, with increasing chain length. The data also show that the alcohol intercalates adopt an interdigitated rather than bilayer arrangement.

Introduction

Intercalation of guest molecules is often studied with layered networks as a means of regulating the interlayer separation and as an initial step in the possible exfoliation of the material to films.[1] Some interesting work with metal phosphonates in this regard has been reported. Specifically, Jacobson and Johnson have studied the imprinting of a binding site for alcohols in layered vanadyl phosphonates.[2] An extension of this work to the regulation of luminescence of a pendant naphthyl group, via alcohol intercalation, in a layered vanadyl phosphonate was reported by Torgerson and Nocera.[3] Poojary and Clearfield have determined the structures of amine intercalates with Zn phenylphosphonate.[4] In these cases, thermal liberation of a species, usually solvent, ligated to the inorganic layers is required to generate a binding site for the intercalant. Typically, this desolvated state is highly moisture sensitive.

Our research group[5] and others[6] have been studying the interesting coordination chemistry of silver(I) sulfonates and their solid-state properties. Sulfonate (RSO_3^-) anions are structurally analogous to phosphonate (RPO_3^{2-}), anions, but they have been much less studied owing to the preconception that they are weakly coordinating ligands. In contrast to the rigid and regular layers observed for metal phosphonates,[7]

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10.1021/ic010800q CCC: $22.00

with transition metal sulfonates, the metal cation is susceptible to partial or even complete hydration, thus prohibiting the formation of a framework solid.[8] Silver(I) sulfonates are an anomaly in that they form very stable nonhydrated layered networks, composed of SO_3 bridges between Ag^I ions, even when isolated from water. A marked difference between this family of compounds and metal phosphonates is that the sulfonate bridging mode in the layer structure, and hence the metal coordination, is variable. For example, a change as minor as going from benzenesulfonate[5b] to *p*-toluenesulfonate[5a] alters the bridging mode of the SO_3 group from μ^6 to μ^5. Silver(I) is noted for its rather pliant coordination sphere, due mainly to a d^{10} electronic configuration, and is able to form stable layered compounds with a range of organosulfonates[5,6a,9] despite individually weaker Ag−O interactions.

There has only been one report of an intercalation study involving a metal sulfonate. In that communication,[5a] Ag *p*-toluenesulfonate was observed to undergo intercalation with nonylamine; however, the exact nature of the host−intercalate interaction and whether intercalation was topotactic were not determined. In this report, we present the intercalation study of Ag trifluoromethanesulfonate, Ag triflate (OTf), with a series of straight chain alcohols. The single-crystal X-ray structure of the ethanol adduct, $[AgOTf\cdot(EtOH)_{0.5}]_\infty$, **1**, is included and shows coordination of the EtOH hydroxyl group to silver(I). The flexibility at the metal center enables coordinative intercalation of alcohols to occur without requiring the thermal liberation of a coordination site. Further to this result is the correlation of the (001) *d*-spacings and calculated *c*-axis lengths, obtained from PXRD data, for the intercalates of longer *n*-chained primary alcohols. These data show a regular increase, directly proportional to the number of carbon atoms in the alkyl chain of the alcohol. Thus, despite having structurally flexible layers, the Ag triflate intercalation is topotactic.

Experimental Section

General Preparation of Ag Triflate−Alcohol Intercalates. All compounds were purchased from Aldrich Chemicals and used without any further purification. For alcohols which were liquid at room temperature, Ag triflate was added directly to the alcohol and sonicated at room temperature to form gels. Crystalline material could be obtained by cooling the gel to 4 °C for several hours. For alcohols which were solids at room temperature, a mixture of Ag triflate and the long chain alcohol was heated in an oven 5 °C above the melting point of the alcohol for 5 min. Upon cooling, off-white crystalline solids were obtained.

Product Analysis. Powder X-ray diffraction (PXRD) data were collected in an ambient air atmosphere on a Scintag XDS2000 diffractometer equipped with a Cu Kα radiation source. A 1° stepping scanning mode in 2θ was employed between 2° and 60°. A suitable PXRD pattern could not be obtained for $AgOTf(EtOH)_{0.5}$ due to loss of guest during analysis. The pattern was generated from the single-crystal data using the SHELXTL '97 XPOW software. TGA and DSC measurements were made using a Netzsch STA 449C simultaneous thermal analyzer, under a nitrogen atmosphere, heating from 25 to 600 °C at a rate of 5 °C per minute.

Table 1. Crystal Data and Refinement Summary for $[AgOTf\cdot(EtOH)_{0.5}]_\infty$, **1**

empirical formula	$C_4H_6F_6S_2O_7Ag_2$, **1**
fw	559.95
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	5.345(7)
b (Å)	11.310(2)
c (Å)	12.004(2)
α (deg)	116.87(1)
β (deg)	90.46(1)
γ (deg)	99.59(1)
V (Å^3)	635.5(8)
Z (molecules/unit cell)	2
D_{calcd} (g/cm^3)	2.926
μ (mm^{-1})	3.516
cryst dimens (mm^3)	0.40 × 0.20 × 0.03
radiation, λ (Å)	0.71073
R_f (sig reflns)[a]	0.0529
R_w (sig reflns)[a]	0.1217

[a] $R_f = (\sum(F_o - F_c)/\sum(F_o)$, $R_w = (\sum\omega(F_o - F_c)^2/\sum\omega(F_o)^2)^{0.5}$.

General X-ray crystallography. Single-crystal X-ray data was collected on a Siemens SMART CCD diffractometer using the ω scan mode ($1.91° < 2\theta < 57.7°$) and solved using the NRCVAX suite of programs.[10] An empirical absorption correction was made using the SADABS routine associated with the Siemens diffractometer. The structure was refined and hydrogen atoms were generated as riding spheres to their parent atoms using the SHELXTL '97 suite of programs.[11]

Single-Crystal Determination of 1. A colorless platelike crystal of dimensions 0.40 × 0.20 × 0.03 mm was employed. The lattice parameters are as follows: $a = 5.345(7)$ Å, $b = 11.310(2)$ Å, $c = 12.004(2)$ Å, $\alpha = 116.87(1)°$, $\beta = 90.46(1)°$, $\gamma = 99.59(1)°$, $V = 635.5(8)$ Å^3, space group $P\bar{1}$, and $Z = 2$. A total of 7474 reflections were measured, and these were merged to give 3228 unique reflections ($R_{merg} = 0.0553$), 1892 of which were considered to be observed when $I > 2.0\sigma(I)$. A summary of pertinent crystal data is presented in Table 1. Final R values for significant data ($R = 5.29\%$, $R_w = 12.17\%$, GOF = 1.111) were obtained for a total of 195 parameters. In the last D-map, the deepest hole was −1.339 e/Å^3 and the highest peak 2.198 e/Å^3, which was closely associated with the Ag center. Fractional atomic coordinates are given in Table 2 and selected bond distances and angles in Table 3.

Results and Discussion

Structure of $AgOTf\cdot(EtOH)_{0.5}$, 1. Single crystals of **1** could be obtained by allowing an ethanolic solution of Ag triflate to slowly evaporate at 4 °C.[12] The structure of **1** is that of a layered motif extending in the *ab* plane with an asymmetric unit composed of two Ag^I cations, two triflate anions, and one molecule of ethanol (Figure 3). The ethyl

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(12) AgOTf was dissolved in ethanol for the purposes of obtaining single crystals. Compound **1** is also attainable via the analogous preparations, without dissolution, employed for the higher analogues.

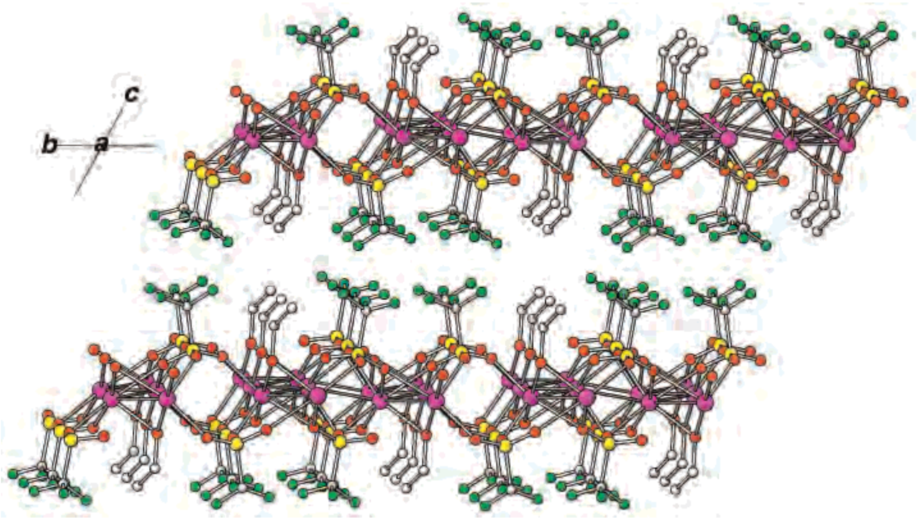

Figure 1. View of the lamellar network formed by AgOTf·$(EtOH)_{0.5}$, **1**, showing the CF_3 and EtOH groups directed into the interlayer region: Ag, pink spheres; S, yellow spheres; O, red spheres; F, green spheres; C, white spheres.

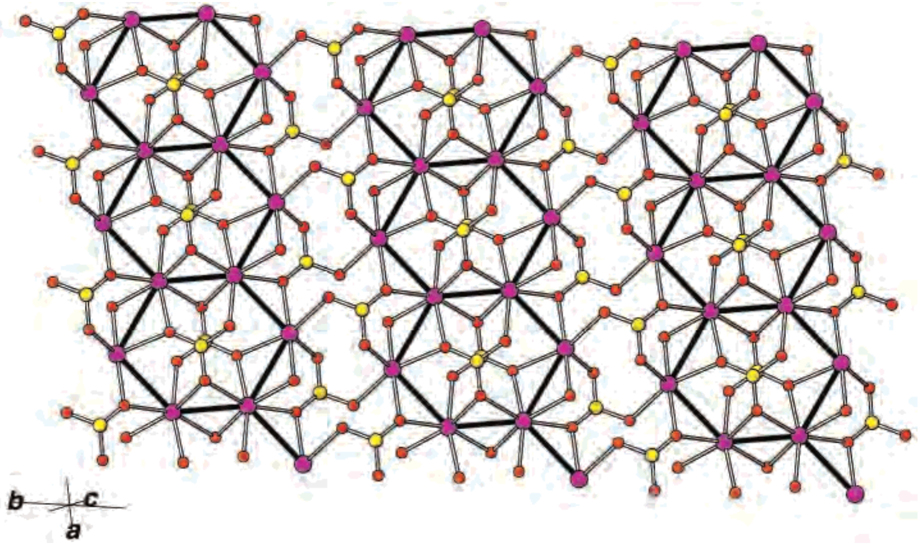

Figure 2. View down onto a single layer of compound **1**. Note the rows of edge-sharing Ag hexagons and the two types (μ^4 and μ^5) of bridging sulfonate groups.

groups from the ethanol and CF_3 groups from the triflate ions are projected into the interlayer region in the direction of the *c*-axis (Figure 1). The interlayer distance, defined as the perpendicular distance between the layers of Ag^I ions, is 10.71(1) Å. The thickness of an individual lamella, defined as the region containing solely the Ag, S, and O atoms, is 3.64(2) Å. The difference between these two values, 7.07(3) Å, constitutes the gallery height in the complex.

The construction of the layer can be considered as being built up from one-dimensional chains of edge-sharing hexagons of Ag ions running along the *a*-axis (Figure 2). The Ag2 atoms constitute the shared edges of the hexagons (Ag2−Ag2a 3.060(1) Å) while the Ag1 centers complete the remaining two corners (Ag1−Ag2 = 3.327(2) Å).[13] Ag1 is seven-coordinate with a coordination sphere composed of four sulfonate oxygen atoms, from four different sulfonate groups (Ag1−O = 2.381(5)−2.546(5) Å), one oxygen atom from ethanol (Ag1−O7 = 2.546(5) Å), and the two contacts to adjacent Ag2 centers. Ag2 is nine-coordinate with a coordination sphere consisting of five sulfonate oxygen atoms, from five different sulfonate groups (Ag2−O = 2.425(5)−2.588(5) Å), an oxygen atom from ethanol (Ag2−

Table 2. Atomic Parameters for Non-Hydrogen Atoms of Compound **1**

	x	*y*	*z*	U_{eq}
Ag(1)	8833(1)	1796(1)	4959(1)	27(1)
Ag(2)	14542(1)	3530(1)	4763(1)	24(1)
S(1)	3737(3)	1550(2)	6675(2)	18(1)
S(2)	19726(3)	4457(2)	3318(2)	18(1)
O(1)	5181(9)	2281(5)	6085(5)	25(1)
O(2)	4479(10)	290(5)	6426(5)	26(1)
O(3)	1027(9)	1453(5)	6542(5)	28(1)
O(4)	18943(9)	5757(5)	3896(5)	24(1)
O(5)	22434(9)	4522(5)	3513(5)	25(1)
O(6)	18127(9)	3416(5)	3517(4)	24(1)
O(7)	12042(9)	1279(5)	3522(5)	23(1)
F(1)	7159(9)	2710(5)	8577(5)	41(1)
F(2)	3485(10)	2049(5)	9000(4)	47(1)
F(3)	4192(11)	3807(5)	8716(5)	53(1)
F(4)	16677(9)	3822(5)	1363(4)	39(1)
F(5)	20494(10)	4737(5)	1304(5)	46(1)
F(6)	19668(11)	2675(5)	983(4)	44(1)
C(1)	4710(14)	2600(7)	8341(6)	26(1)
C(2)	19126(14)	3892(7)	1641(6)	25(1)
C(3)	11189(14)	682(8)	2196(7)	30(2)
C(4)	13310(15)	852(9)	1445(8)	37(2)

Table 3. Selected Bond Distances and Angles for Compound **1**[a]

bond	length (Å)	bond	length (Å)
Ag(1)−Ag(2)d	3.327(2)	Ag(2)−Ag(2)a	3.060(1)
Ag(1)−O(1)	2.381(5)	Ag(1)−O(3)	2.432(5)
Ag(1)−O(7)	2.393(5)	Ag(1)−O(4)	2.530(5)
Ag(1)−O(2)	2.546(5)	Ag(2)−O(5)d	2.588(5)
Ag(2)−O(6)	2.425(5)	Ag(2)−O(7)	2.427(5)
Ag(2)−O(4)	2.467(5)	Ag(2)−O(5)e	2.528(5)
S(1)−O(1)	1.451(5)	S(1)−O(2)	1.443(5)
S(1)−O(3)	1.437(5)	S(2)−O(4)	1.451(5)
S(2)−O(5)	1.449(5)	S(2)−O(6)	1.448(5)

bond	angle (deg)	bond	angle (deg)
O(1)−Ag(1)−O(7)	169.8(2)	O(1)−Ag(1)−O(3)a	93.8(2)
O(7)−Ag(1)−O(3)a	96.14(18)	O(1)−Ag(1)−O(4)b	91.68(16)
O(7)−Ag(1)−O(4)b	91.0(2)	O(3)a−Ag(1)−O(4)b	87.19(17)
O(1)−Ag(1)−O(2)c	78.99(17)	O(7)−Ag(1)−O(2)c	95.36(18)
O(3)a−Ag(1)−O(2)c	110.77(17)	O(4)b−Ag(1)−O(2)c	160.09(15)
O(1)−Ag(1)−Ag(2)d	51.19(12)	O(7)−Ag(1)−Ag(2)d	120.35(13)
O(3)a−Ag(1)−Ag(2)d	139.08(13)	O(4)b−Ag(1)−Ag(2)d	75.20(12)
O(2)c−Ag(1)−Ag(2)d	85.33(12)	O(6)−Ag(2)−O(7)	100.00(17)
O(6)−Ag(2)−O(4)b	165.30(16)	O(7)−Ag(2)−O(4)b	91.75(17)
O(6)−Ag(2)−O(5)e	83.94(17)	O(7)−Ag(2)−O(5)e	160.10(16)
O(4)b−Ag(2)−O(5)e	88.01(17)	O(6)−Ag(2)−O(5)d	87.81(17)
O(7)−Ag(2)−O(5)d	93.16(16)	O(4)b−Ag(2)−O(5)d	82.71(16)
O(5)e−Ag(2)−O(5)d	106.54(14)	O(6)−Ag(2)−Ag(2)b	83.13(11)
O(7)−Ag(2)−Ag(2)b	145.41(12)	O(4)b−Ag(2)−Ag(2)b	82.18(11)
O(5)e−Ag(2)−Ag(2)b	54.17(11)	O(5)d−Ag(2)−Ag(2)b	52.36(11)
O(6)−Ag(2)−Ag(1)a	62.82(13)	O(7)−Ag(2)−Ag(1)a	82.21(13)
O(4)b−Ag(2)−Ag(1)a	128.23(12)	O(5)e−Ag(2)−Ag(1)a	82.35(12)
O(5)d−Ag(2)−Ag(1)a	148.65(11)	Ag(2)b−Ag(2)−Ag(1)a	127.75(5)
Ag(2)b−O(4)−Ag(1)b	86.13(15)	Ag(2)e−O(5)−Ag(2)a	73.46(13)
Ag(1)−O(7)−Ag(2)	90.13(18)		

[a] The equivalent positions are as follows: (1) *x y z*, (2) −*x* −*y* −*z*. The lattice is primitive. There are no centering vectors.

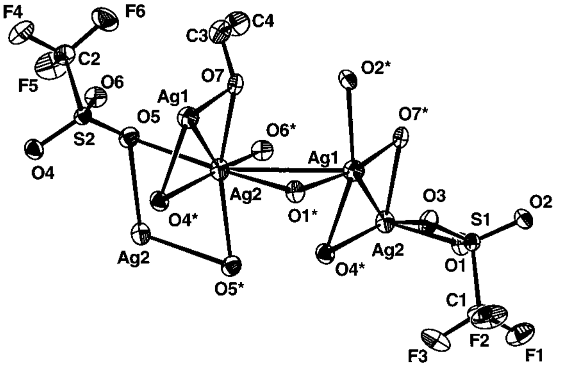

Figure 3. ORTEP plot of **1** showing the numbering scheme and the complete coordination spheres of Ag1 and Ag2. Thermal ellipsoids of 50% probability are represented.

O7 = 2.427(5) Å), and three contacts to adjacent Ag centers, two to Ag1 and a third to another Ag2 at the previously stated distances. Both Ag centers have irregular geometries. The layer structure in **1** is essentially a cross between the layer structures observed in Ag *p*-toluenesulfonate,[5a] which has seven-coordinate metal centers, and in Ag benzenesulfonate, which has nine-coordinate metal centers.[5b] Of the two types of triflate groups, one caps each face of the Ag hexagons and the other cross-links the rows of hexagons. Overall, the capping sulfonate group has a μ^5-bridging mode where oxygen atoms O4 and O5 both bridge two Ag centers (O4−Ag1 2.530(5) Å, O4−Ag 2.467(5) Å, O5−Ag2 2.528(5) Å, O5−Ag2a 2.588(5) Å). O6 is only singly coordinated to Ag2 (O6−Ag2 2.425(5) Å) and cannot bridge to Ag1 like O4 due to the tilting of the triflate away from the *ab* plane (O6−Ag1 3.102(5) Å). For the cross-linking triflate group, overall, the coordination is μ^4, where O1 bridges two Ag centers (O1−Ag1 2.381(5) Å, O1−Ag2 2.610(5) Å) and O2 and O3 each form a single bond to different Ag centers (O2−Ag1 2.546(5) Å, O3−Ag1 2.432(5) Å). The EtOH guests are coordinated, through the hydroxyl oxygen in a μ^2 bridging mode, to Ag1 and Ag2 (O7−Ag1 = 2.393(5) Å, O7−Ag2 = 2.427(5) Å). The distance between adjacent chains in the *y*-direction, as measured by the shortest Ag−Ag distance, is approximately 4.47 Å. Triflate ions are not uncommonly observed in singly, doubly or triply bridging coordination modes,[14] and, to our knowledge, the highest degree of bridging observed for a triflate ion is 4. This 4-fold bridging mode occurs in silver(I) complexes of certain polyaromatic

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(13) For the current work, connections between Ag centers are to indicate distances under van der Waals contact distances and not necessarily imply any "argentophilic" interactions. For works concerning such interactions, see: (a) Che, C.-M.; Tse, M.-C.; Chan, M. C. W.; Cheung, K.-K.; Phillips, D. L.; Leung, K.-H. *J. Am. Chem. Soc.* **2000**, *122*, 2464. (b) Omary, M. A.; Webb, T. R.; Assefa, Z.; Shankle, G. E.; Patterson, H. H. *Inorg. Chem.* **1998**, *37*, 1380. (c) Rawashdeh-Omary, M. A.; Omary, M. A.; Patterson, H. H. *J. Am. Chem. Soc.* **2000**, *122*, 10371. (d) Wang, Q.-M.; Mak, T. C. W. *J. Am. Chem. Soc.* **2000**, *122*, 7608. (e) Wang, Q.-M.; Mak, T. C. W. *J. Am. Chem. Soc.* **2001**, *123*, 1501. (f) Wang, Q.-M.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 1130.

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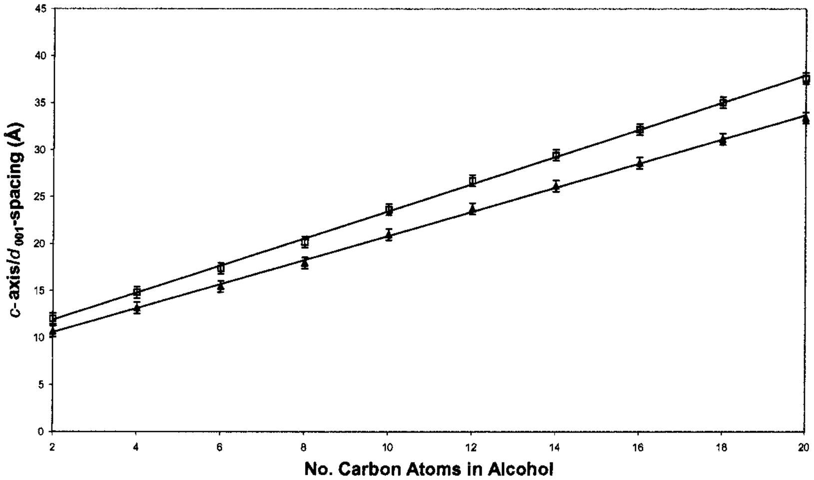

Figure 4. Plot of interlayer spacing, *d* (triangles), and calculated *c*-axis lengths (squares) versus number of carbons in the straight chain alcohol intercalate showing the linear relationships.

ligands and serves to form 1-D columns of SO_3-bridged silver centers.[15] In **1**, the combination of the μ^4 triflate ion, which bridges the Ag hexagons, and the unprecedented μ^5 triflate ion, which caps the hexagons, serves to generate a stable two-dimensional network.

Preparation of Intercalation Complexes. The intercalation ability of AgOTf was further probed using primary straight-chained alcohols containing an even number of carbon atoms ranging from C_4H_9OH to $C_{20}H_{41}OH$. In all cases, polycrystalline solids were obtained. Intercalation products were obtained either by the direct addition of 0.5 equiv of the alcohol to AgOTf or by dissolving the alcohol in ethyl acetate initially. Regardless of the method of synthesis, the isolated intercalation products, with the same alcohol, gave material with identical PXRD patterns.[16] Significantly, no preliminary drying of AgOTf was required to liberate a coordination site for the alcohols. This is attributed to the weakly coordinating triflate ion altering its coordination mode to accommodate the alcohol guest.

Thermal Analysis of AgOTf and Intercalates. The TGA of a sample of AgOTf shows no mass loss prior to 383 °C. However, DSC data show that prior to the mass loss, there are two endothermic phase changes, at 280 and 323 °C. Significantly, both of these endotherms are completely reversible. This observation corroborates the fact that no thermal pretreatment of the AgOTf is required and that the layers are able to reorient. The intercalate complexes show mass losses close to the boiling points of their respective alcohols.

PXRD of AgOTf and Intercalates. 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[17] for each of the intercalates increases linearly, from 10.66(2) Å for EtOH$\supset$AgOTf to 33.11(2) Å for $C_{20}H_{41}OH\supset$AgOTf, in direct proportion to the number of carbon atoms in the alcohol, indicating that the AgOTf layers are being pushed further apart by the longer alcohols (Figure 4). This correlation can be extended further to the calculation of *c*-axis lengths for each of the intercalates.[18] Again, a linear relationship is obtained, indicating that the remaining crystallographic parameters for the intercalates are very similar to those determined for AgOTf·$(EtOH)_{0.5}$.[19] In **1**, the distance between symmetry-related EtOH oxygen atoms, O7, on opposite sides of a layer following the *c*-axis, is 8.22(2) Å. *Summing this value with the ideal O−C_{term} distances for the other alcohols, assuming all-trans conformations, gives the distances corresponding to the principal Bragg peak in the PXRD for each of the intercalates* (Table 4). Thus, it may be deduced that (i) the longer chain alcohols are coordinating to the Ag layers in a

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(15) Ino, I.; Wu, L. P.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Sakai, R. *Inorg. Chem.* **2000**, *39*, 5430.

(16) Treatment of AgOTf with 1.0, 1.5, or 2.0 equiv of the respective alcohols all gave PXRD patterns which matched the intercalation products formed with 0.5 equiv of alcohol. However, high C, H elemental analyses on these samples indicated that there was most likely other alcohol included in the interlayer in a noncoordinative fashion.

(17) d_{001} values reported are an average of those calculated from each pattern (eq 1):

$$\bar{d}_{001} = \frac{\sum_{i=1}^{k} n d_{00n}}{k} \tag{1}$$

(18) Values for *c* were calculated as follows. For triclinic systems:

$$V = abc\sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma} \tag{2}$$

If it is assumed that all the unit cell parameters remain the same as for AgOTf·$(EtOH)_{0.5}$ and only *c* is variable upon intercalation, then eq 3 can be inserted into eq 2 to give a direct relationship between *c* and d_{001} (eq 4).

$$c^* = \frac{ab \sin \gamma}{V} \tag{3}$$

$$d^*_{001} = c^* = \frac{\sin \gamma}{d_{001}\sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}} \tag{4}$$

Inputting the angular data for AgOTf·$(EtOH)_{0.5}$ leads to the reduced relationship (eq 5).

$$c = (1.126)d_{001} \tag{5}$$

Table 4. Comparison of the Observed d_{001} Distances and the d_{001} Distances Calculated Assuming a Topotactic Intercalation of Alcohols for $[\mathrm{AgOTf(ROH)_{0.5}}]_\infty$

intercalated alcohol	d_{001} (Å ± 0.02) PXRD (obsd)	length of ROH O−C_{term} (Å)[a]	d_{001} (Å ± 0.02) PXRD (calcd)[b]	absolute difference (Å)
C_4H_9OH	13.14	4.86	13.08	0.05
$C_6H_{13}OH$	15.42	7.36	15.58	0.16
$C_8H_{17}OH$	17.92	9.86	18.08	0.16
$C_{10}H_{21}OH$	20.96	12.36	20.58	0.38
$C_{12}H_{25}OH$	23.71	14.86	23.08	0.63
$C_{14}H_{29}OH$	26.13	17.35	25.57	0.56
$C_{16}H_{33}OH$	28.57	19.85	28.07	0.50
$C_{18}H_{35}OH$	31.11	22.74	30.96	0.15
$C_{20}H_{39}OH$	33.37	25.34	33.56	0.19

[a] Reference 20. [b] Reference 21.

manner analogous to that in **1**; (ii) the alkyl chains of the alcohols orient along an axis parallel to the *c*-axis in **1**; (iii) the alcohols adopt an interdigitated, rather than bilayer, arrangement within the interlayer region; (iv) intercalation of straight chain alcohols with AgOTf is topotactic despite the layers lacking a rigid structure.

Conclusions

The first systematic intercalation study of a metal sulfonate network has been presented. The structural flexibility offered by the weaker Ag−sulfonate interactions allows topotactic intercalation of alcohols to occur without any thermal pretreatment of the layered network. The crystal structure of **1** confirms that the intercalation is coordinative and also shows the triflate ion to adopt an unprecedented μ^5 coordination mode.

Acknowledgment. This research was funded by Imperial Oil Ltd. and the Natural Sciences and Engineering Research Council (NSERC) of Canada in the form of a CRD grant and a scholarship to A.P.C.

Supporting Information Available: Graphical powder X-ray diffraction data of AgOTf and its intercalates. An X-ray crystallographic file for compound **1**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The intercalate PXRD patterns suffer from major orientation effects and are dominated by low-order reflections. Owing to the strong interdependence of crystallographic parameters for triclinic crystal systems, this data was incomplete, even when α, β, and γ were constrained close to those obtained for $\mathrm{AgOTf{\cdot}(EtOH)_{0.5}}$, and attempts to index these data to obtain unit cell parameters for the intercalates were unsuccessful.

(20) These lengths were determined using MM2 calculations: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

(21) These values were obtained by summing the ideal chain length of the alcohol with the trans-layer O7−O7 distance of 8.22(2) Å.