3282 *Chem. Mater.* **1998,** *10,* 3282−3283

Silver Sulfonates: An Unexplored Class of Layered Solids

George K. H. Shimizu,[*,†] Gary D. Enright,
Chris I. Ratcliffe, Gabriela S. Rego,
Jennifer L. Reid, and John A. Ripmeester*

Steacie Institute for Molecular Sciences,
National Research Council of Canada,
Ottawa, Ontario, K1A 0R6, Canada

Received June 5, 1998
Revised Manuscript Received August 18, 1998

Inorganic lamellar solids occur in many forms with an equally broad range of applications. Widely studied classes include clays,[1] metal chalcogenides,[2] and metal oxides[3] as well as the metal phosphates[4] and phosphonates.[4a,5] Clays and metal phosphonates have been extensively studied due to their ability to intercalate guest molecules and the concurrent swelling of their interlayer regions which accompanies these intercalation processes.[6] Herein, we present a family of previously unrecognized layered complexes. Silver sulfonates represent an unexplored class of lamellar solids[7] which, owing to their strong analogy to zirconium phosphonates, offer a potential wealth of chemical opportunity.[8] We report the single-crystal X-ray structure of silver *p*-toluenesulfonate, AgOTs, an infinite lamellar array containing SO_3-bridged Ag^I centers. Correlation to the powder X-ray diffraction pattern (PXRD) confirms the single crystal to be representative of the bulk sample. DSC/TGA data and results of preliminary intercalation experiments with nonylamine are presented.

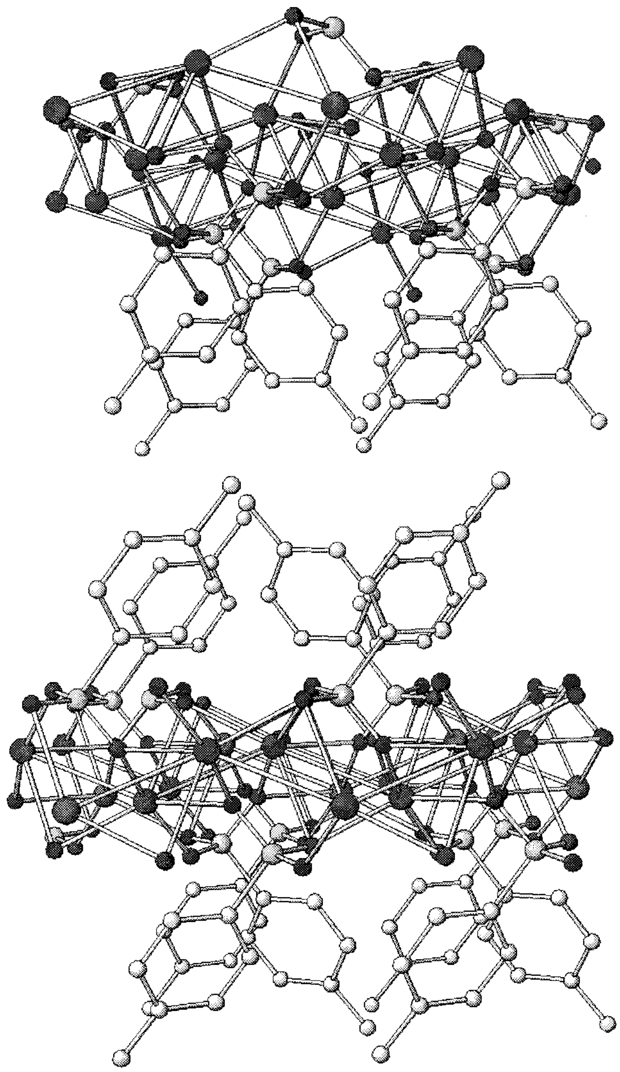

Figure 1. Perspective view of AgOTs, showing the infinite lamellar structure and toluene groups directed into the interlayer region.

Diffusion of isopropyl ether into a methanol solution of pure Ag *p*-toluenesulfonate[9] resulted in the growth of platelike, colorless crystals. A single-crystal X-ray determination[10] revealed an infinite lamellar structure consisting of parallel layers of SO_3-bridged silver ions with the toluene groups directed into the interlamellar region (Figure 1). These features are exactly analogous to a layered metal phosphonate. The interlayer distance, defined as the perpendicular distance between planes of silver ions, is 15.309 (1) Å, and the thickness of a single lamella, defined as the Ag−O−S layers, is 3.90 (1) Å. Thus, the gallery height present in the compound is 11.41 (2) Å. Adjacent layers align down the *a* axis, which is not perpendicular to the lamellae, corresponding to an offset of 0.99 (1) Å. The coordina-

---

[†] Present adress: Department of Chemistry, University of Calgary, 2500 University Drive N. W., Calgary, Alberta, T2N 1N4 Canada. Phone: 1-403-220-5347. Fax: 1-403-289-9488. E-mail: gshimizu@ucalgary.ca.

(1) Occelli, M. A.; Robson, H. *Expanded Clays and Other Microporous Solids*; Academic Press: New York, 1992.

(2) Whittingham, M. S. *Prog. Solid State Chem.* **1978**, *12*, 41.

(3) Jacobsen, A. J. *Solid State Chemistry Compounds*; Cheetham, A. K., Day, P. Eds.; Clarendon, Oxford, 1992; pp 182−233.

(4) (a) Cao, G.; Hong, H.-G.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, *25*, 420. (b) Clearfield, A.; Costantino, U. *Comprehensive Supramolecular Chemistry;* Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Elsevier Science: New York, 1996; Vol. 7, Chapter 4, pp 107−151.

(5) Alberti, G. *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Elsevier Science: New York, 1996; Vol. 7, Chapter 5, pp 151−189.

(6) (a) Cao, G.; Garcia, M. E.; Alacá, M.; Burgess, L. F.; Mallouk, T. E. *J. Am. Chem. Soc.* **1992**, *114*, 7574. (b) Burwell, D. A.; Thompson, M. E. *Chem. Mater.* **1991**, *3*, 730. (c) Carlino, S. *Solid State Ionics* **1997**, *98*, 73. (d) Zhang, B.; Clearfield, A. *J. Am. Chem. Soc.* **1997**, *119*, 2751.

(7) The structure of silver *p*-chlorobenzenesulfonate (Bernardinelli, G.; Lucken, E. A. C.; Costines, M. *Z. Kristallogr.* **1991**, *195*, 145−146) is isomorphous with the structure reported herein. However, in the previous work, no mention of the two-dimensional nature of the compound was made. Only tables of unit cell parameters, atomic coordinates, and data acquisition conditions were presented.

(8) (a) For a previous attempt at the generation of a layered sulfonate, see: Kosnic, E. J.; McClymont, E. L.; Hodder, R. A.; Squattrito, P. J. *Inorg. Chim. Acta* **1992**, *201*, 143. (b) For a AgOTs−*p*-aminobenzoic acid complex, see: Smith, G. E.; Lynch, D. E.; Kennard, C. H. L. *Inorg. Chem.* **1996**, *35*, 2711−2712.

(9) Obtained from Aldrich Chemical Co. and used as received.

(10) Crystal data for AgOTs: $C_7 H_7 Ag S O_3$, fw = 279.06 g mol^{-1}, colorless needles, monoclinic, space group $P2_1/c$, $a = 15.3410(9)$ Å, $b = 6.0145(3)$ Å, $c = 8.5605(5)$ Å, $\beta = 93.69(1)°$, $V = 788.23(8)$ Å^3, $Z = 4$, $D_c = 2.352$ g cm^{-3}, $R = 3.3\%$, $R_w = 3.2\%$, and GOF = 1.87 for 137 parameters using 1668 ($F_o > 2.5\,\sigma(F_o)$) reflections. Mo Kα radiation ($\lambda = 0.71073$ Å), μ(Mo Kα) = 1.04 mm^{-1}. Data collection temperature = −100 °C. The structure was collected on a Siemens SMART CCD diffractometer using the ω scan mode (3° < 2θ < 57.4°) and solved using the NRCVAX suite of programs. Gabe, E. J.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Cryst.* **1989**, *22*, 384.

10.1021/cm980409b CCC: $15.00

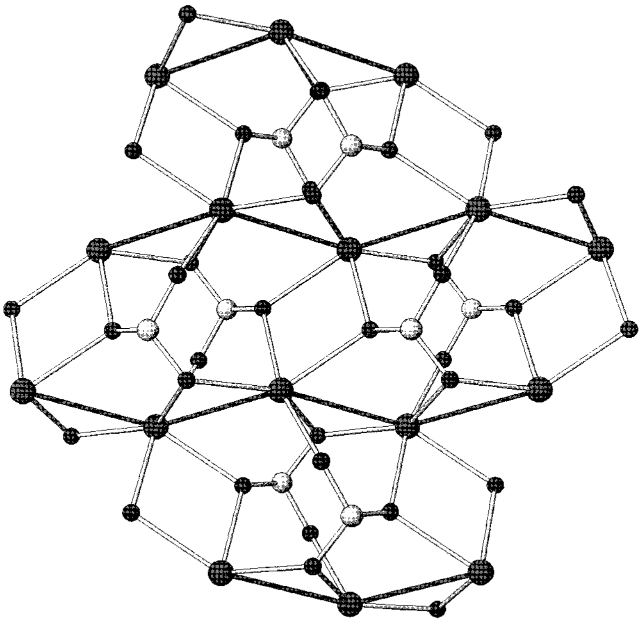

Figure 2. View down onto a single layer of AgOTs, with the toluene groups omitted for clarity, showing the 5-fold donacity of the SO_3 groups and the seven-atom coordination about each silver. Ag, large dark circles; S, light circles; O, small dark circles.

tion exhibited in this structure by both the Ag^I ion and the sulfonate ligand is quite unusual (Figure 2). Each Ag^I ion has no fewer than seven other atoms within van der Waals distance,[11] namely two other Ag^I ions (Ag−Ag distance = 3.350 (2) Å and five sulfonate oxygen atoms (four Ag−O distances range from 2.391 (3) to 2.524 (3) and a single long contact at 2.699 (3) Å).[12] The geometry at the Ag^I centers is best described as the insertion of an additional donor atom to one of the rectangular faces in a trigonal prismatic structure, similar to the geometry in TaF_7^{2-}.[13] This elevated coordination about the silver center results from each individual sulfonate group forming bonds to five different Ag^I ions, with two oxygen atoms each bonding to two different silver centers while the third oxygen bonds to only a single silver ion.[14] The PXRD pattern of the bulk sample of AgOTs could be indexed with unit cell parameters which match the single-crystal parameters at room temperature.[15] Cross-polarization magic-angle spinning (CPMAS) solid-state ^{13}C NMR also confirmed that only a single type of toluenesulfonate group was present in the bulk structure, as was observed crystallographically.

DSC/TGA analyses of a sample of AgOTs revealed that the sample was completely stable to almost 250 °C.[16] As could be expected, a lamellar structure composed of monovalent cations interacting with monovalent anions does not yield a framework with a stability equivalent to complexes composed of di- or trivalent ions interacting with one another. However, this stability is notable as the compound is purported to be highly air and light sensitive.

Numerous lamellar networks are known to intercalate organic molecules and swell in their presence.[6] Direct treatment of AgOTs with 2 equiv of liquid nonylamine results in the formation of a waxy solid. Upon heating at 70 °C for 30 min, this material shows a room-temperature PXRD pattern indicative of a layered solid with an interlayer spacing of 24.46(1) Å.[17] The length of an *all-trans*-nonylamine molecule is ca. 12.3 Å. Currently, we cannot say whether the Ag/SO_3 layers retain the same structural form. A systematic study to elucidate the nature of this intercalation behavior is in progress. The structural versatility and promising intercalation behavior of this novel lamellar system indicates a wealth of lower temperature (<250 °C) applications for which layered silver sulfonates may find use. Preliminary results concerning other silver organosulfonates reveal that the lamellar motif is a general phenomenon.[18]

Acknowledgment. We thank Carol Bowes and Jamie Bennett, for assistance with the PXRD, and Chris Tulk and Rudi Branderhorst, for their help with the DSC samples. Ann Webb of NRC's Institute of Biological Sciences is acknowledged for performing the elemental analyses.

Supporting Information Available: Full single-crystal data, observed/simulated PXRD data, and ^{13}C CPMAS NMR spectra for AgOTs as well as observed PXRD pattern and solid state ^{13}C CPMAS NMR spectra for AgOTs·$(C_9H_{19}NH_2)_2$ (30 pages). Ordering information is given on any current masthead page.

CM980409B

---

[11] Moore and co-workers have recently performed a comprehensive search of the Cambridge Structural Database to quantify occurrences of metal ion geometries; see: Venkataraman, D.; Du, Y.; Wilson, S. R.; Zhang, P.; Hirsch, K.; Moore, J. S. *J. Chem. Ed.* **1997**, *74*, 915. Their results, available at http://sulfur.scs.uiuc.edu, indicate quantitatively that silver(I) most commonly adopts three- and four-coordinate geometries.

[12] Van der Waal's contacts for Ag−Ag and Ag−O are 3.42 and 3.52 Å, respectively.

[13] Muetterties, E. L.; Wright, C. M. *Quart. Rev.* **1967**, *21*, 109.

[14] This is a highly unusual mode of coordination for a R−SO_3 anion: Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

[15] As the measured PXRD pattern was obtained at 25 °C, the single crystal data were recollected at room temperature. The crystallographically determined unit cell for AgOTs at 25 °C was a = 15.4015(9) Å, b = 6.0465(3) Å, c = 8.6201(5) Å, β = 93.051(1)°, V = 801.61(8) Å^3. Indexing of the PXRD pattern, using 31 lines, gave a matching unit cell.

[16] Heating of a sample of AgOTs at a rate of 5 °C min^{-1} revealed a baseline signal up until 245.6 °C, at which point a reversible endothermic phase transition (10.25 kJ mol^{-1}) was observed. A second irreversible endothermic phase change (5.48 kJ mol^{-1}), with an onset temperature of 298.2 °C, was then observed prior to a large exothermic process at ca. 325 °C associated with a mass loss of 43.4%.

[17] Treatment of AgOTs with 2 equiv of liquid nonylamine at 25 °C gave a PXRD pattern with a number of peaks at very small values of θ; however, the pattern did not resemble that of a layered material. DSC revealed a phase change at ca.. 50 °C. A sample heated to 70 °C for 30 min and then cooled to room temperature gave a PXRD pattern which was indexed, using the 15 most intense lines, to the following unit cell, a = 8.82(1) Å, b = 24.46(1) Å, c = 6.27(1) Å, β = 95.49(1)°, V = 1346(1) Å^3. Elemental analyses confirmed a 2:1 stoichiometry of amine to AgOTs for both 25 and 70 °C samples.

[18] Ag benzenesulfonate also forms a layered network: Shimizu, G. K. H.; Enright, G. D.; Ratcliffe, C. I.; Ripmeester, J. A. Unpublished results.