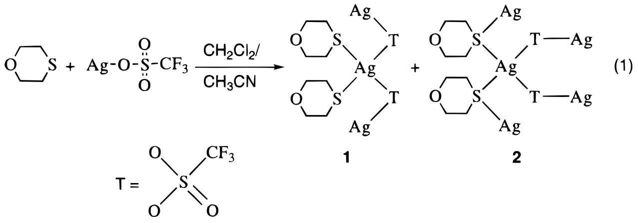
Two Types of New Polymeric Silver(I) Complexes from 1,4-Thioxane and Silver Triflate

Herwig A. Buchholz,* G. K. Surya Prakash,* Julian F. S. Vaughan, Robert Bau, and George A. Olah

Donald P. and Katherine B. Loker Hydrocarbon Research
Institute and Department of Chemistry, University of
Southern California, Los Angeles, California 90089-1661

Received February 5, 1996

The propensity for d^{10} Ag^+ cations to form coordination complexes with a variety of ligands (*e.g.* S, P, N, and O) is well documented.[1] Presently, there is a great deal of interest in stable coordination compounds between the soft Lewis acid Ag^+ and ligands containing soft sulfur atoms. Most of this research has focused on macrocyclic thioethers.[2−5] Here we describe the preparation and single-crystal X-ray structures of two distinct novel polymeric silver(I) complexes containing tetracoordinated Ag^+ centers. One involves silver(I) cations bound to two 1,4-thioxane and two bridging triflate (CF_3SO_3) anions whereas the second has bridging through both 1,4-thioxane sulfur and triflate oxygen atoms.



(1)

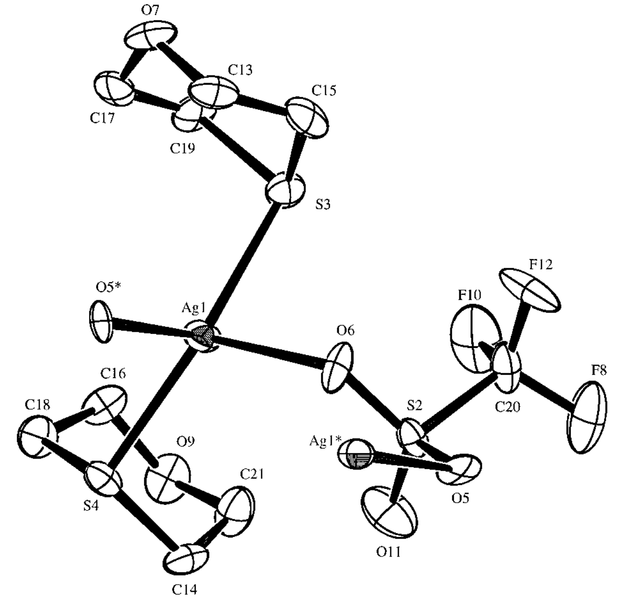


Figure 1. A portion of the structure of the chain polymer **1**.

1,4-Thioxane was reacted with silver triflate, at ambient temperature, in a 1:1 mixture of dichloromethane and acetonitrile (eq 1). On slow evaporation of the solvent in an argon atmosphere, colorless crystals were isolated and shown to be of two discrete silver complexes, **1** and **2**. Dissolving silver triflate (1.00 g, 3.9 mmol) in an excess of 1,4-thioxane (1.22 g, 11.7 mmol), using sonication, led to a complex which was obtained in pure form by crystallization at −78 °C and removal of excess 1,4-thioxane under reduced pressure. The material was assigned by NMR and IR spectroscopy to the structure of complex **2**. The ^1H NMR showed two triplets of equal intensity. The signal corresponding to the methylene protons α to sulfur (2.8 ppm) were low-field-shifted by 0.2 ppm, when compared to those of 1,4-thioxane. This is due to decreased shielding by complexation of the sulfur. The other signal for the protons next to oxygen was identical to that of 1,4-thioxane. Accordingly, the ^{13}C NMR spectrum showed two methylene resonances, both shifted to lower field by 1.3 ppm (CH_2S) and 0.3 ppm (CH_2O), relative to 1,4-thioxane. Complex **1** could not be prepared selectively by altering the reaction stoichiometry.

Complex **1** (Figure 1) crystallizes as colorless prisms, which were found to be air sensitive. The silver atom is tetracoordinated by the sulfur atoms of two 1,4-thioxane molecules and the oxygen atoms of two triflate ligands, giving in the crystal an infinite one-dimensional-chain polymer with bridging only through the triflate moieties, $[Ag^+(CF_3SO_3)^-{\cdot}2(1,4\text{-thioxane})]_n$.[6] As expected, the 1,4-thioxane rings retain the lower energy chair conformations and a stereoview of **1** (Supporting Information) clearly shows the "zigzagging" backbone of the infinite polymer. The chains are discrete, with no linking interactions. The high selectivity of Ag^+ for sulfur is demonstrated by the absence of any coordination to the oxygen nonbonding electron pairs of the mixed cyclic ether 1,4-thioxane. Complex **2** crystallizes as colorless plates.[7] The results of an X-ray analysis (Figure 2) showed that, while the immediate coordination around the silver(I) ion is similar [a single silver(I) cation bound to two 1,4-thioxane and two triflate ligands], the overall arrangement is that of an infinite two-dimensional lattice. Bridging between silver(I) cations occurs *via* the participation of *both* sulfur nonbonded electron pairs of a 1,4-thioxane unit and two oxygen atoms from a single triflate moiety, giving the structure depicted in Figure 2. Complex **2**, unlike **1**, was not air-sensitive, possibly due to the silver(I) cations being protected by the two-dimensional lattice in $[Ag^+(CF_3SO_3)^-{\cdot}1,4\text{-thioxane}]_n$.

The capacity of both sulfur nonbonded electron pairs, in thioethers, to bridge Ag^+ cations has been reported.[2,4,5,8] Recent

---

(1) For examples see: (a) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press Inc.: New York, 1984. (b) Amoroso, A. J.; Jeffery, J. C.; Jones, P. L.; McCleverty, J. A.; Psillakis, E.; Ward, M. D. *J. Chem. Soc., Chem. Commun.* **1995**, 1175. (c) Michaelides, A.; Skoulika, S.; Kiritis, V.; Aubry, A. *J. Chem. Soc., Chem. Commun.* **1995**, 1415.

(2) Küppers, H.-J.; Wieghardt, K.; Tsay, Y.-H.; Krüger, C.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 575.

(3) Blake, A. J.; Gould, R. O.; Reid, G.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1990**, 974.

(4) Blake, A. J.; Collison, D.; Gould, R. O.; Reid, G.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1993**, 521.

(5) Clarkson, J.; Yagbasan, R.; Blower, P. J.; Rawle, S. C.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1987**, 950.

(6) The structure for **1** was determined by direct methods and refined on F for all 1604 independent reflections measured at 153 K with a Siemens P4 diffractometer (Cu Kα radiation) ($2\theta_{max} = 100°$). $R(F) = 0.048$ and $R_w(F) = 0.053$ for 1453 reflections with $F > 4\sigma(F)$.

(7) Analysis for **2** ($C_{10}H_{16}Ag_2F_6O_8S_4$): ^1H NMR ($CDCl_3$) δ 2.8 (t, $J_{H,H}$ 4.5 Hz, CH_2S), 3.9 (t, $J_{H,H}$ 4.5 Hz, CH_2O); ^{13}C NMR ($CDCl_3$) δ 28.3 (CH_2S), 68.4 (CH_2O), 120.3 (q, $J_{C,F}$ 318 Hz, CF_3); IR (NaCl plates, cm^{-1}) 3010−3040 (C−H, w), 639 (C−S, s), 1105 (C−O, s), 811 (C−C, s), 969 (C−C, s), 1009 (C−C, s), 1276 (C−F, s). The structure was determined by direct methods and refined on F to the final agreement factors of $R(F) = 0.083$ and $R_w(F) = 0.087$ for 1694 reflections with $F > 4\sigma(F)$.

(8) Norén, B.; Oskarsson, A. *Acta Chem. Scand., Ser. A* **1984**, *38*, 479.

(9) Solov'ev, V. N.; Chekhlov, A. N.; Zabirov, N. G.; Martynov, I. V. *Dokl. Chem. (Engl. Transl.)* **1995**, *341*, 502.

S0020-1669(96)00123-1 CCC: $12.00

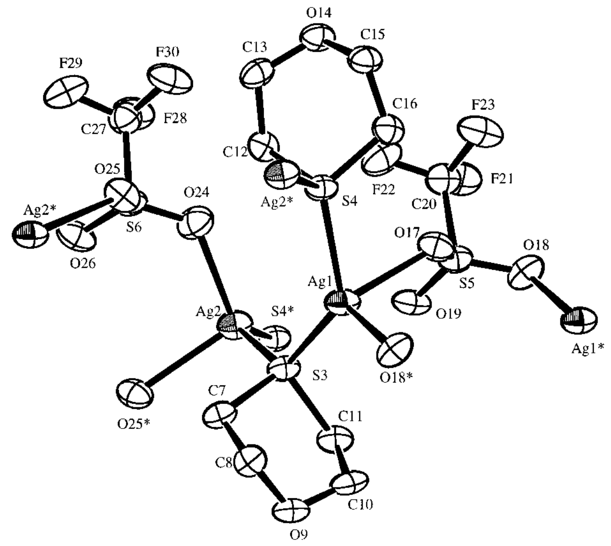


Figure 2. A portion of the structure of the infinite polymer **2**.

Table 1. Selected Distances (Å) and Angles (deg) for $[C_9H_{16}AgF_3O_5S_3]_n$ (**1**)

Ag(1)−S(3)	2.482(3)	Ag(1)−O(5*)	2.591(7)
Ag(1)−S(4)	2.465(3)	Ag(1)−O(6)	2.474(7)

S(4)−Ag(1)−S(3)	144.7(1)	S(3)−Ag(1)−O(5*)	118.9(2)
S(4)−Ag(1)−O(6)	115.8(2)	S(4)−Ag(1)−O(6)	88.2(2)
O(6)−Ag(1)−O(5*)	83.8(2)		

Table 2. Crystallographic Data for $[C_9H_{16}AgF_3O_5S_3]_n$ (**1**)

fw = 465.3	space group $P2_1/n$
$a = 9.793(3)$ Å	$T = -120$ °C
$b = 9.446(2)$ Å	$\lambda = 1.541\ 78$ Å
$c = 16.934(4)$ Å	$\rho_{calc} = 3.97$ g cm^{-3}
$\beta = 96.13(2)°$	$R(F) = 4.80\%$
$V = 1557.5(7)$ Å^3	$R_w(F) = 5.34\%$
$Z = 4$	$\mu = 29.2$ mm^{-1}

Table 3. Selected Distances (Å) and Angles (deg) for $[C_{10}H_{16}Ag_2F_6O_8S_4]_n$ (**2**)

Ag(1)−S(3)	2.472(7)	Ag(2)−S(3)	2.516(6)
Ag(1)−S(4)	2.565(6)	Ag(2)−S(4*)	2.455(7)
Ag(1)−O(17)	2.475(17)	Ag(2)−O(24)	2.371(18)
Ag(1)−O(18*)	2.406(17)	Ag(2)−O(25*)	2.480(19)

Ag(1)−S(3)−Ag(2)	126.0(3)	S(4)−Ag(1)−O(18*)	95.0(5)
Ag(1)−S(4)−Ag(2*)	124.1(3)	S(3)−Ag(2)−O(24)	107.2(4)
S(3)−Ag(1)−S(4)	134.4(2)	S(3)−Ag(1)−O(18*)	123.2(5)
S(3)−Ag(2)−S(4*)	129.1(2)	S(3)−Ag(2)−O(24)	96.9(5)
O(24)−Ag(2)−O(25*)	100.8(6)	S(3)−Ag(2)−O(25*)	97.8(4)
O(17)−Ag(1)−O(18*)	101.1(6)	S(4*)−Ag(2)−O(24)	123.3(5)
S(4)−Ag(1)−O(17)	85.8(4)	S(4*)−Ag(2)−O(25*)	101.6(4)

Table 4. Crystallographic Data for $[C_{10}H_{16}Ag_2F_6O_8S_4]_n$ (**2**)

fw = 722.2	space group $I2/a$
$a = 20.362(4)$ Å	$T = -120$ °C
$b = 7.921(2)$ Å	$\lambda = 1.541\ 78$ Å
$c = 25.990(5)$ Å	$\rho_{calc} = 2.327$ g cm^{-3}
$\beta = 100.36(3)°$	$R(F) = 8.33\%$
$V = 4123.5(15)$ Å^3	$R_w(F) = 8.75\%$
$Z = 8$	$\mu = 19.9$ mm^{-1}

work by Reid[10] described unique structural features of the polymeric silver(I) complex obtained after reaction of $AgBF_4$ with $MeS(CH_2)_3SMe$. In this case, the two sulfur atoms coordinated differently, one with both nonbonded electron pairs and the other with only one. In polymer **2**, no monodentate sulfur ligation was observed.

Weak Ag−S interactions have been observed in silver macrocyclic thioether complexes (usually around 3 Å);[4] however, there was no evidence for this phenomenon in either complex **1**, Ag(1)−S(4) 2.465(3) to Ag(1)−S(3) 2.482(3) Å (Table 1), or **2**, Ag(2)−S(4*) 2.463(7) to Ag(1)−S(4) 2.569(7) Å (Table 3). Complex **2** displays some variation in the Ag−S bond lengths, as well as in the bond angles [S−Ag−S 129.3(2)−134.1(2)°] (Table 3), which could be due to steric strain within the structure.[9]

An initial study of the reactivity of complex **2** involved its reaction with 1,3-diiodo- and 1,3-dibromopropane, at ambient temperature, in acetonitrile. This competition experiment showed the much higher reactivity of diiodopropane toward **2**. ^{13}C NMR spectra (DMSO-d_4 and acetonitrile-d_3) showed the formation of a disulfonium salt containing two 1,4-thioxane moieties bridged by the C_3 linkage. Full characterization of the dication will be reported elsewhere.

To our knowledge, **1** and **2** are the first examples of polymeric silver(I) cation complexes with coordination to two sulfur and two oxygen ligands. The formation and chemistry of related systems are under investigation.

Acknowledgment. Support by the Loker Hydrocarbon Research Institute and the National Science Foundation is gratefully acknowledged.

Supporting Information Available: A figure showing a stereoview of **1** and tables of crystal data, positional parameters, bond distances and angles, and thermal parameters for **1** and **2** (17 pages). Ordering information is given on any current masthead page.

IC960123D

---

(10) Black, J. R.; Champness, N. R.; Levason, W.; Reid, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1277.