3236 *Inorg. Chem.* **1998,** *37,* 3236−3242

Nitrogen Base Adducts with Silver(I) *p*-Toluenesulfonate: Syntheses and Single Crystal X-ray Characterizations of the Adducts with Pyridine (1:1), 2-Aminopyridine (1:2), 2-Aminopyrimidine (1:1), 4,6-Dimethyl-2-aminopyrimidine (2:3), and 3-Aminobenzoic Acid (1:2) and the Crystal Structure of the Parent Silver(I) *p*-Toluenesulfonate

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The complex adducts of silver(I) *p*-toluenesulfonate, [Ag(pts)], with the nitrogen bases pyridine (1:1), $[\{Ag(pts)\}(py)]_n$ (**2**), 2-aminopyridine (2:4), $[\{Ag(pts)\}_2(2\text{-}apy_4)]$ (**3**), 2-aminopyrimidine (1:1), $[\{Ag(pts)\}(2\text{-}ap)]_n$ (**4**), 4,6-dimethyl-2-aminopyrimidine (2:3), $[\{Ag(pts)\}_2(dmap)_3]_n$ (**5**), and 3-aminobenzoic acid (2:4), $[\{Ag(pts)\}_2(3\text{-}aba)_4]$ (**6**), have been prepared and their structures, together with that of the parent compound, silver(I) *p*-toluenesulfonate (**1**), determined by X-ray diffraction. Crystals of **1** ($C_{14}H_{14}Ag_2O_6S_2$) are monoclinic, space group $P2_1/a$, $Z = 2$, with $a = 8.596(3)$ Å, $b = 6.0330(4)$ Å, $c = 15.363(4)$ Å, and $\beta = 93.03(1)°$. The polymeric structure is based on bis(sulfonato-(*O,O′*) bridged dimers analogous to those found in some of the O,O′-bridged silver(I) carboxylates, these also having pseudo trigonal bipyramidal AgO_4 centers. All sulfonate oxygens are utilized in coordination. The structures of the monoheteroaromatic nitrogen donor group adducts (**2**, **3**, and **6**) are either polymeric [**2** ($C_{12}H_{12}AgNO_3S$): AgN_2O_2 centers] or discretely dimeric [**3** ($C_{34}H_{38}Ag_2N_8O_6S_2$) and **6** ($C_{42}H_{42}Ag_2N_4O_{14}S_2$): both AgN_2O_2] and can be considered the result of replacement of either one or two oxygen sites about the silver in [Ag(pts)] by nitrogen donors, with subsequent rearrangement about very distorted tetrahedral silver centers. For **2**, crystals are monoclinic, space group $P2_1$, $Z = 2$, with $a = 9.1237(8)$ Å, $b = 5.553(1)$ Å, $c = 12.439(1)$ Å, and $\beta = 91.182(8)°$. For **3**, crystals are triclinic, space group $P\bar{1}$, $Z = 1$, with $a = 8.635(3)$ Å, $b = 10.434(3)$ Å, $c = 11.138(3)$ Å, $\alpha = 104.89(2)$, and $\beta = 90.20(2)°$, $\gamma = 99.94(2)°$. For **6**, crystals are monoclinic, space group $P2_1/a$, $Z = 4$, with $a = 8.006(2)$ Å, $b = 31.675(8)$ Å, $c = 8.803(2)$ Å, and $\beta = 104.413(9)°$. Hydrogen-bonding interactions via the second functional group in both **3** and **6** give additional lattice stability. However, with the bifunctional heteroaromatic pyrimidines, extension of the polymer structures occurs through both ring nitrogens to give either a simple ribbon polymer (**4**, $C_{11}H_{12}AgN_3O_3S$) (trigonal planar $AgON_2$ repeat) or a pyrimidine-linked, sulfonate-bridged eight-membered cyclic dimer unit, in which the tetrahedral $Ag_2O_2N_2$ centers incorporate an additional unidentate pyrimidine (**5**, $C_{32}H_{41}Ag_2N_9O_6S_2$). For **4**, crystals are monoclinic, space group $P2_1/n$, $Z = 4$, with $a = 6.535(2)$ Å, $b = 7.3440(8)$ Å, $c = 26.13(1)$ Å, and $\beta = 90.44(1)°$: For **5**, crystals are monoclinic, space group $C2/c$, $Z = 4$, with $a = 21.312(6)$ Å, $b = 10.650(1)$ Å, $c = 17.565(5)$ Å, and $\beta = 110.58(1)°$. Hydrogen bonding is also significant in lattice stabilization in both of these structures. The preparation of an unstable adduct of Ag(pts) with aniline, $[\{Ag(pts)\}(an)_3]$ **7**, is also reported, and infrared spectroscopy indicates that it is has both amine-bonded aniline as well as uncoordinated aniline.

Introduction

In a program of investigation in our laboratory of the nature of the adducts of silver(I) *p*-toluenesulfonate with nitrogen bases, initial results suggested that their behavior would be analogous to that of the Lewis base adducts of the silver(I) halides.[1] The first of these silver compounds, isolated as the only product from the reaction of silver(I) *p*-toluenesulfonate with 4-aminobenzoic acid, *catena*-[{4-aminobenzoic acid}−4-toluenesulfonato-(*O,O′,O″*)silver(I)], was reported in a previous communication.[2] The structure comprises a network polymer based upon a distorted tetrahedral AgO_3N center involving three oxygens from independent sulfonate residues and an amine nitrogen from the 4-aminobenzoic acid adduct molecule. Since the structures of only silver(I) methanesulfonate, silver(I) bromomethanesulfonate, and silver(I) 2-pyridinesulfonate are

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(1) (a) AgCl−quinoline (1:1): Mills, N. K.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1984**, 225−228. (b) AgBr−2-methylpyridine (1:2), AgBr−3-methylpyridine (1:1), AgBr−4-methylpyridine (1:1): Healy, P. C.; Mills, N. K.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 111−116. (c) AgI−piperidine (1:1): Ansell, G. B. *J. Chem. Soc. B* **1971**, 443−446. (d) AgI−morpholine (1:1): Ansell, G. B. *J. Chem. Soc., Perkin Trans. 2* **1976**, 104−106. (e) AgI−triethylamine (1:1), AgI−2-methylpyridine (1:1), AgI−3-methylpyridine (1:1), AgI−4-methylpyridine (1:1), AgI−quinoline (1:1): Healy, P. C.; Mills, N. K.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 1851−1864.

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Table 1. Crystal Data for [{Ag(pts)}$_2$]$_n$ (**1**), [{Ag(pts)}(py)]$_n$ (**2**), [{Ag(pts)}$_2$(2-apy)$_4$] (**3**), [{Ag(pts)}(2-ap)]$_n$ (**4**), [{Ag(pts)}$_2$(dmap)$_3$]$_n$ (**5**), and [{Ag(pts)}$_2$(3-aba)$_4$] (**6**)

	1	**2**	**3**
empirical formula	$C_{14}H_{14}Ag_2O_6S_2$	$C_{12}H_{12}AgNO_3S$	$C_{34}H_{38}Ag_2N_8O_6S_2$
fw	550.6	358.2	934.6
space group	$P2_1/a$ (No. 14)	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)
T (°C)	25	25	25
λ (Å)	0.710 73	0.710 73	0.710 73
a (Å)	8.596(3)	9.1237(8)	8.635(3)
b (Å)	6.0330(4)	5.553(1)	10.434(3)
c (Å)	15.363(4)	12.439(1)	11.138(3)
α (deg)	90	90	104.89(2)
β (deg)	93.03(1)	91.182(8)	90.20(2)
γ (deg)	90	90	99.94(2)
V (Å^3)	795.6(4)	630.1(2)	954.1(5)
Z	2	2	1
ρ_{obsd} (g cm^{-3})	2.34	1.90	1.64
ρ_{calcd} (g cm^{-3})	2.330	1.888	1.627
μ (cm^{-1})	27.5	17.6	11.9
$R(F_o)^a$	0.090	0.017	0.025
$R_w(F_o^2)^b$	0.216	0.044	0.065

	4	**5**	**6**
empirical formula	$C_{11}H_{12}AgN_3O_3S$	$C_{32}H_{41}Ag_2N_9O_6S_2$	$C_{42}H_{42}Ag_2N_4O_{14}S_2$
fw	374.2	927.6	1106.7
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P2_1/a$ (No. 14)
T (°C)	25	25	25
λ (Å)	0.71073	0.71073	0.71073
a (Å)	6.535(2)	21.312(6)	8.006(2)
b (Å)	7.3440(8)	10.650(1)	31.675(8)
c (Å)	26.13(1)	17.565(5)	8.803(2)
β (deg)	90.44(1)	110.58(1)	104.413(9)
V (Å^3)	1254.2(7)	3732(2)	2162.1(9)
Z	4	4	2
ρ_{obsd} (g cm^{-3})	1.96	1.65	1.72
ρ_{calcd} (g cm^{-3})	1.982	1.651	1.700
μ (cm^{-1})	17.8	12.2	10.8
$R(F_o)^a$	0.065	0.041	0.028
$R_w(F_o^2)^b$	0.231	0.115	0.075

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ {with $w = \sigma^2(F_o^2) + (AP)^2 + BP$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$}.

known,[3] it was decided to include the structure determination of the parent compound silver(I) *p*-toluenesulfonate [Ag(pts)] **1** as a guide to the processes involved in the replacement of coordination sites on the silver center by the nitrogen base donors. The set of bases chosen were the aromatic compounds pyridine (py), 2-aminopyridine (2-apy), 2-aminopyrimidine (2-ap), 4,6-dimethyl-2-aminopyrimidine (dmap), 3-aminobenzoic acid (3-aba), and aniline (an), a series of unsubstituted and substituted aromatic nitrogen base donors, some with the potential for secondary hydrogen-bond interactions to enhance crystal stability. These compounds provided a series which represented an extension of the original study involving the (1:1) complex adduct of [Ag(pts)] with 4-aminobenzoic acid.[2] In addition, the bases used were mainly solids, minimizing the instability problems commonly associated with the silver(I) halide−Lewis base adducts, necessitating special handling techniques because of crystal instability. The 2-aminopyrimidine compounds are of particular interest as adduct formers because of their demonstrated ability to form very stable hydrogen-bonded chain arrays via their stereochemically associative amino and hetero ring nitrogens.

Reported here are the preparations of the adducts of silver(I) *p*-toluenesulfonate with the Lewis bases pyridine, [{Ag(pts)}(py)]$_n$ (**2**), 2-aminopyridine, [{Ag(pts)}$_2$(2-apy)$_4$] (**3**), 2-aminopyrimidine, [{Ag(pts)}(2-ap)]$_n$ (**4**), 4,6-dimethyl-2-aminopyrimidine, [{Ag(pts)}$_2$(dmap)$_3$]$_n$ (**5**), and 3-aminobenzoic acid, [{Ag(pts)}$_2$(3-aba)$_4$] (**6**), and their structural characterizations using single-crystal X-ray diffraction methods and infrared spectroscopy. The crystal structure of the parent compound silver(I) *p*-toluenesulfonate, [{Ag(pts)}$_2$]$_n$ (**1**), was also determined by X-ray diffraction while a sixth adduct from the series, that with aniline, [{Ag(pts)}(an)$_3$] (**7**) was prepared but its structure determination by X-ray methods was not possible because of crystal instability.

Experimental Section

Preparation. Complex adducts of silver(I) *p*-toluenesulfonate with pyridine (1:1), (**2**), 2-aminopyridine (1:2) (**3**), 2-aminopyrimidine (1:1) (**4**), and aniline (**7**) were prepared by adding 0.1 g of the nitrogen base to 40 cm^3 of a saturated ethanolic solution of silver(I) *p*-toluenesulfonate at ambient temperature. The solutions were then allowed to evaporate almost to dryness at room temperature over a period of several days, giving crystalline products (**2**, colorless needles; **3** and **4**, colorless plates; **7**, brown needles). Compound **4** was unusual in that a white solid precipitated almost immediately upon combination of the reactant, and the formation of hard colorless prismatic crystals subsequently occurred within the bulk of this residue. Complexes with 4,6-dimethyl-2-aminopyrimidine (2:3), (**5**) and 3-aminobenzoic acid (1:2) (**6**) were prepared by refluxing 1:1 stoichiometric quantities of silver(I) *p*-toluenesulfonate (2 mmol) and the appropriate nitrogen base (2 mmol) in ethanol (30 cm^3) for 10 min. The product from the preparation of **6**, a white solid that rapidly precipitated, was removed and redissolved in methanol, and the solution was allowed to partially

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(3) (a) Silver(I) methanesulfonate: Charbonnier, F.; Faure, R.; Loiseleur, H. *Acta Crystallogr*. **1977**, *B33*, 2824−2826. (b) Silver(I) bromomethanesulfonate: Charbonnier, F.; Faure, R.; Loiseleur, H. *Acta Crystallogr*. **1978**, *B34*, 3598−3601. (c) Silver(I) 2-pyridinesulfonate: Charbonnier, F.; Faure, R.; Loiseleur, H. *Cryst. Struct. Commun*. **1981**, *10*, 1129−1132.

Table 2. Bond Lengths (Å) and Angles (deg) for the Coordination Polyhedra in Compounds **1**−**6**

(a) Bond Distances

Compound **1**			
Ag(1)−O(1)	2.448(6)	Ag(1)−O(3)^{b}	2.401(6)
Ag(1)−O(2)^{a}	2.418(6)	Ag(1)−O(1)^{a}	2.547(7)
$a = -x, 1 - y, 1 - z$: $b = -{}^1/_2 - x, -{}^1/_2 + y, 1 - z$			
Compound **2**			
Ag(1)−O(1A)	2.551(3)	Ag(1)−O(3A)^{b}	2.277(3)
Ag(1)−O(1A)^{a}	2.618(3)	Ag(1)−N(1B)	2.241(3)
$a = 1 - x, {}^1/_2 + y, -z$; $b = x, 1 + y, z$			
Compound **3**			
Ag(1)−O(1A)	2.559(2)	Ag(1)−N(1B)	2.210(2)
Ag(1)−O(1A)^{a}	2.596(2)	Ag(1)−N(1C)	2.203(2)
$a = 1 - x, -y, 1 - z$			
Compound **4**			
Ag(1)−O(11A)	2.41(1)	Ag(1)−N(3B)^{a}	2.25(1)
Ag(1)−N(1B)	2.29(1)		
$a = 1 + x, y, z$			
Compound **5**			
Ag(1)−O(12C)	2.384(4)	Ag(1)−N(1B)	2.267(4)
Ag(1)−O(13C)^{a}	2.500(4)	Ag(1)−N(1A)	2.268(4)
$a = 1 - x, y, {}^1/_2 - z$			
Compound **6**			
Ag(1)−O(11A)	2.441(2)	Ag(1)−N(31B)	2.238(3)
Ag(1)−O(11A)^{a}	2.627(2)	Ag(1)−N(31C)	2.285(3)
$a = -x, -y, -z$			

(b) Bond Angles

Compound **1**			
O(1)−Ag(1)−O(2)^{a}	89.6(2)	O(2)^{a}−Ag(1)−O(3)^{b}	99.4(2)
O(1)−Ag(1)−O(3)^{b}	164.8(2)	O(2)^{a}−Ag(1)−O(1)^{a}	132.4(2)
O(1)−Ag(1)−O(1)^{a}	72.3(2)	O(3)^{b}−Ag(1)−O(1)^{a}	92.7(2)
Compound **2**			
O(1A)−Ag(1)−O(1A)^{a}	88.7(1)	O(1A)^{a}−Ag(1)−O(3A)^{b}	90.6(1)
O(1A)−Ag(1)−O(3A)^{b}	95.8(1)	O(1A)^{a}−Ag(1)−N(1B)	99.2(1)
O(1A)−Ag(1)−N(1B)	92.1(1)	O(3A)^{b}−Ag(1)−N(1B)	167.5(1)
Compound **3**			
O(1A)−Ag(1)−O(1A)^{a}	75.32(7)	O(1A)^{a}−Ag(1)−N(1B)	115.65(7)
O(1A)−Ag(1)−N(1B)	92.86(8)	O(1A)^{a}−Ag(1)−N(1C)	99.95(8)
O(1A)−Ag(1)−N(1C)	115.38(8)	N(1B)−Ag(1)−N(1C)	139.48(8)
Compound **4**			
O(11A)−Ag(1)−N(1B)	95.9(3)	N(1B)−Ag(1)−N(3B)^{b}	130.5(3)
O(11A)−Ag(1)−N(3B)^{b}	133.6(3)		
Compound **5**			
O(12C)−Ag(1)−O(13C)^{a}	105.1(1)	O(13C)^{a}−Ag(1)−N(1B)	101.8(1)
O(12C)−Ag(1)−N(1B)	110.2(1)	O(13C)^{a}−Ag(1)−N(1A)	106.5(1)
O(12C)−Ag(1)−N(1A)	105.8(1)	N(1B)−Ag(1)−N(1A)	125.7(1)
Compound **6**			
O(11A)−Ag(1)−O(11A)^{a}	82.7(1)	O(11A)^{a}−Ag(1)−N(31B)	96.1(1)
O(11A)−Ag(1)−N(31B)^{a}	134.7(1)	O(11A)^{a}−Ag(1)−N(31C)	107.4(1)
O(11A)−Ag(1)−N(31C)	95.8(1)	N(31B)−Ag(1)−N(31C)	126.9(1)

evaporate at room temperature in the dark, giving pale brown flattened prisms, while colorless needle crystals of **5** were obtained from the original reaction mixture after several days' standing. Infrared spectroscopy, melting points, and elemental analyses (C, H, N) were used as indicators of adduct formation. [Anal. Found for **2**: C, 40.5; H, 3.4; N, 3.7. Calc for $C_{12}H_{12}AgNO_3S$: C, 40.2; H, 3.4; N, 3.9. Found for **3**: C, 43.8; H, 4.1; N, 12.0. Calc for $C_{34}H_{38}Ag_2N_8O_6S_2$: C, 43.7; H, 4.1; N, 12.0. Found for **4**: C, 34.8; H, 3.2; N, 11.2. Calc for $C_{11}H_{12}AgN_3O_3S$: C, 35.2; H, 3.2; N, 11.2. Found for **5**: C, 41.5; H, 4.3; N, 13.7. Calc for $C_{32}H_{41}Ag_2N_9O_6S_2$: C, 41.4; H, 4.5; N, 13.7. Found for **6**: C, 45.3; H, 3.7; N, 4.9. Calc for $C_{42}H_{42}Ag_2N_4O_{14}S_2$: C, 45.6; H, 3.8; N, 5.1. Found for **7**: C, 54.6; H, 5.2; N, 7.8. Calc for $C_{25}H_{28}AgN_3O_3S$: C, 53.8; H, 5.1; N, 7.5].

Data Collection, and Structure Solution and Refinement. Single-crystal X-ray diffraction data were collected at ambient temperature (25 °C) on an Enraf-Nonius CAD-4 diffractometer (monochromatic Mo Kα radiation, $\lambda = 0.710\,73$ Å) and were corrected both for absorption, using semiempirical methods,[4] and for extinction. Crystal data and other numerical details of structure determination and refinement are given in Table 1. Structures were solved by either Patterson or direct methods (SHELXS-86[5]) and refined (on F^2), with all non-hydrogen atoms anisotropic (SHELXL-93[6]). Hydrogen atoms, particularly those involved in hydrogen-bonding associations, were located by difference methods, but generally these were included at calculated positions and their positional and thermal parameters refined as riding models. Final residuals are defined as follows: The absolute

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(6) Sheldrick, G. M. *SHELXL-93: Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1993.

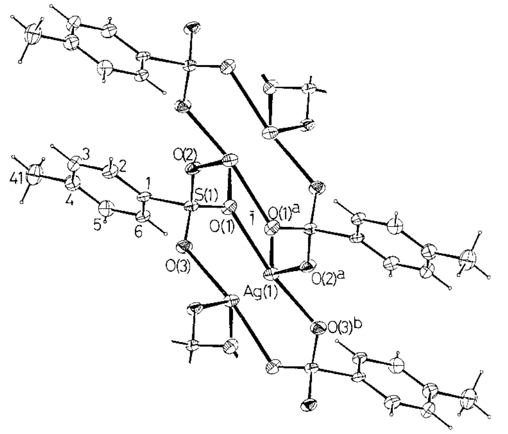

Figure 1. Atom-numbering scheme and molecular structure of the dimeric repeating unit in part of the step-polymer in the complex of silver(I) *p*-toluenesulfonate $[\{Ag(pts)\}_2]_n$ (**1**). Atoms are carbon unless otherwise indicated and are shown as 20% probability ellipsoids.

configuration for the chiral complex with pyridine $[\{Ag(pts)(py)]_n$ (**2**) was determined by the method of Flack[7] [absolute structure parameter 0.01(3)]. With the parent compound (**1**), the refinement residual of 0.090 could not be improved upon despite data re-collection and re-refinement. This is generally attributable to the poor data, the reason being the uncompromising needlelike crystal morphology having no transverse cleavage. Also, as a consequence, a large residual peak in the final difference map (ca. 2.4 e Å^{-3}) was found adjacent to the silver, but was not considered structurally significant. The structure obtained was not disordered in any way and is of sufficient precision to allow a meaningful discussion to be made.

Discussion

$[\{Ag(pts)\}_2]_n$ (1). The polymeric structure of silver(I) *p*-toluenesulfonate (**1**) is based on bis(sulfonato-(O,O′)-bridged dimer units [Ag(1)−O(1), 2.448(6) Å; Ag−O(3)^b, 2.401(6) Å ($b = -^1/_2 - x$, $-^1/_2 + y$, $1 - z$)]. These dimer units have symmetry related by the *a*-glide operation, giving an Ag- - -Ag separation of 3.3704(7) Å (Table 2). The pseudo trigonal bipyramidal AgO_4 stereochemistry about each Ag is completed by a bidentate sulfonato-(O,O′) association [Ag(1)−O(1)^a, 2.547(7) Å; Ag−O(2)^a, 2.418(6) Å ($a = -x$, $1 - y$, $1 - z$)] (Figure 1). The Ag - -Ag separation across the inversion center is 3.3703(7) Å. In many respects, this structure is analogous to the type 4 dimer−polymer[8] (in which the dimer is linked into a step-polymer via bis-linkages to the axial site of the silver), found with reasonable incidence among the silver(I) carboxylates,[9] e.g., silver(I) oxalate, silver(I) perfluorobutyrate, silver(I) malonate, and silver(I) glycolate hemihydrate. However, the major differences are that the Ag−O bond distances in **1** are not only longer but also more equidimensional than in the silver carboxylates where Ag−O(axial) and Ag−O(equatorial) are typically 2.2−2.3 and 2.4−2.5 Å, respectively.[8] The Ag- - -Ag distance is also considerably longer than in the carboxylates (2.78−3.05 Å), which, in addition, usually have inversion symmetry or pseudosymmetry in the dimer units. With **1**, the step-polymer chains extend down the *a* axis of the unit cell, with no intermolecular or interchain associations across the *c* cell direction. It is also worthy of note that this example is the only one among the silver(I) *p*-toluenesulfonate series reported here in which the bidentate sulfonato-(O,O′) interaction is found, although the bidentate bridging mode is of higher incidence, e.g., compounds **2** and **5**.

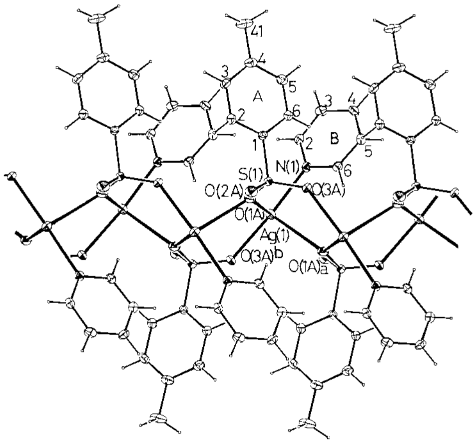

Figure 2. Atom-numbering scheme and molecular structure for the complex polymer $[\{Ag(pts)\}(py)]_n$ (**2**).

$[\{Ag(pts)\}(py)]_n$ (2). In the structure of the 1:1 adduct of silver(I) *p*-toluenesulfonate with pyridine $[\{Ag(pts)\}(py)]_n$, the chain polymer structure of the parent is rearranged and results in a chiral polymer extending along the crystallographic 2_1 screw axis of the monoclinic unit cell (Figure 2). Replacement of only one site in the distorted tetrahedral AgO_4 silver coordination center by a pyridine nitrogen [Ag(1)−N(1B), 2.241(3) Å] is probably the maximum possible stereochemically while retaining the basic silver sulfonate framework. This Ag−N bond distance compares with 2.32(1) Å in the structure of tetrahedral tetrakis(pyridine)silver(I) perchlorate[10] and 2.37(1) Å in the 1:1 silver(I) benzoate−pyridine adduct.[11] The remaining three sites about Ag in the present structure are occupied by oxygens from independent sulfonate residues [Ag−O(1A), 2.551(3) Å; Ag−O(1A)^a, 2.618(3) Å ($a = 1 - x$, $^1/_2 + y$, $-z$); Ag−O(3A)^b, 2.277(3) Å ($b = x$, $1 + y$, z)]. The structure is analogous to the first reported nitrogen base adduct of silver(I) *p*-toluenesulfonate with 4-aminobenzoic acid (4-aba), $[\{Ag(pts)\}(4\text{-}aba)]_n$,[2] in which the amine nitrogen donor inserts in the distorted tetrahedral coordination sphere of silver. However, the absence of any additional interactive groups on the pyridine adduct molecule means that there are no secondary inter- or intramolecular associations stabilizing the polymer chains.

$[\{Ag(pts)\}_2(2\text{-}apy)_4]$ (3). The 2:1 adduct of 2-aminopyridine with silver(I) *p*-toluenesulfonate, $[\{Ag(pts)\}_2(2\text{-}apy)_4]$ (**3**), is based on a centrosymmetric complex dimer unit with the two silver atoms bridged by a single sulfonate oxygen [Ag(1)−O(1A), 2.559(2); Ag(1)−O(1A)^a, 2.596(2) Å; Ag(1)−O(1A)−Ag(1)^a, 75.3(8)° ($a = 1 + x$, y, z)] (Figure 3). The Ag- - -Ag separation is 4.078(1) Å. The remaining two coordination sites about the very distorted tetrahedral AgN_2O_2 centers are occupied by the hetero nitrogens of the two 2-apy adduct molecules [Ag(1)−N(1B), 2.210(2) Å; Ag(1)−N(1C), 2.203(3) Å]. The angle range about the tetrahedron is 75.32(7)−139.48(8)° (mean, 106.3°). Intra- and intermolecular hydrogen-bonding associations involving the amine groups of both 2-apy molecules stabilize the lattice [N(21B)−H(21B)- - -O(3A), 2.978(5) Å, N−H- - -O, 153(3)°; N(21C)−H(22C)- - -O(1A), 3.052(5) Å,

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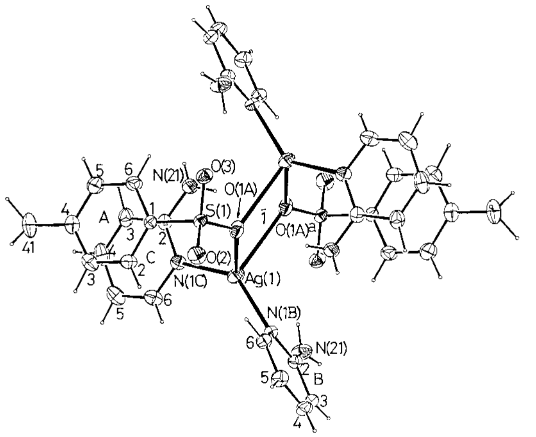

Figure 3. Atom numbering scheme and molecular structure for the dimer [{Ag(pts)}$_2$(2-apy)$_4$] (**3**).

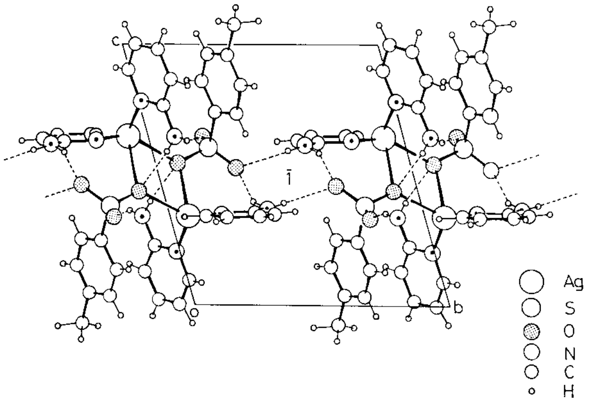

Figure 4. Packing of **3** in the unit cell viewed down the *b* axis, showing the hydrogen-bonding interactions (as broken lines).

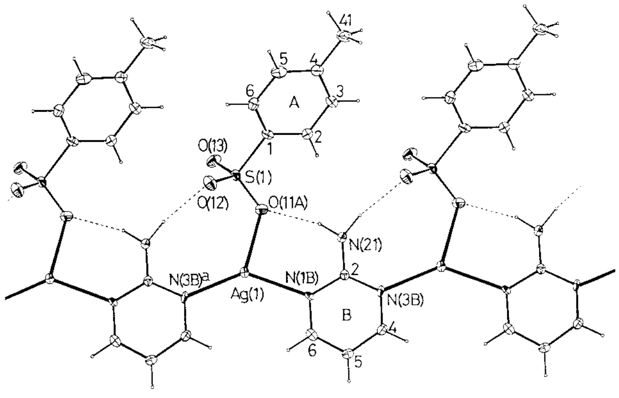

Figure 5. Atom-numbering scheme and molecular structure for the complex polymer [{Ag(pts)}(2-ap)]$_n$ (**4**).

N−H- - -O, 171(3)°] (Figure 4). Intermolecular hydrogen bonds are also found between the amine group and the sulfonate oxygens linking the complex dimers across inversion centers [N(21C)-H(21C)- - -O(2A), 2.977(5) Å, N−H- - -O, 155(3)°; N(21B)−H(22B)- - -O(3A), 3.004(5) Å, N−H- - -O, 168(3)°].

[{Ag(pts)}(2-ap)]$_n$ (4). The 1:1 adduct of silver(I) *p*-toluenesulfonate with 2-aminopyrimidine, [{Ag(pts)}(2-ap)]$_n$, represents the simplest structure among those reported in this set of Ag(pts) compounds. The basic repeat is a distorted trigonal planar three-coordinate AgON$_2$ unit (Figure 5), which comprises a unidentate association to a single *p*-toluenesulfonate oxygen [Ag(1)−O(11A), 2.42(1) Å] and two to independent pyrimidine hetero nitrogens [Ag(1)−N(1B), 2.29(1) Å; Ag(1)−N(3B)^a, 2.25(1) Å (a = 1 + *x*, *y*, *z*)]. Angles about the silver center are 95.9, 130.3, and 133.7(2)°. The extension in the *a* cell direction is stabilized by hydrogen-bonding associations through the 2-amino substituent of the pyrimidine [N(21B)−H(21B)- - -O(11A), 2.955(7) Å, N−H- - -O, 163(3)°; N(21B)−H(22B)- - -O(12A), 2.978(7) Å, N−H- - -O, 168(3)°]. This phenomenon is common among the 2-ap adducts with the tetracarboxylate-bridged copper(II) dimer−polymers, e.g. copper acetate−2-ap (2:1),[12] copper (2-chlorophenoxy)acetate−2-ap (2:1),[13] and copper (2-acetylphenoxy)acetate−2-ap (2:1),[14] in all cases giving symmetrical lateral hydrogen bonding to carboxylate oxygens in zigzag chain polymers. However, compound **4** represents the first adduct of its type with silver(I).

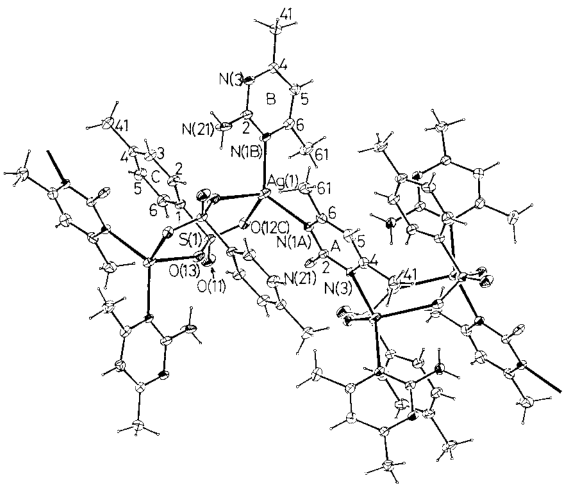

Figure 6. Atom-numbering scheme and molecular structure for the complex dimer−polymer [{Ag(pts)}$_2$(dmap)$_3$]$_n$ (**5**).

[{Ag(pts)}$_2$(dmap)$_3$]$_n$ (5). The structure of the 2:3 complex adduct of silver(I) *p*-toluenesulfonate with 4,6-dimethyl-2-aminopyrimidine, [{Ag(pts)}$_2$(dmap)$_3$]$_n$, has no similarity to either that of the adduct of Ag(pts) with the parent 2-aminopyrimidine (**4**) or to those of any of the other adducts reported here. Instead, centrosymmetric cyclic eight-membered rings comprise the basic molecular repeating unit (Figure 6), each containing two silver centers bridged by two sulfonato-O,O′ groups of two *p*-toluenesulfonate residues (molecule C) [Ag(1)−O(12C), 2.384(4) Å; Ag(1)−O(13C)^a, 2.500(4) Å (a = 1 − *x*, *y*, $^1/_2$ − *z*)]. The tetrahedral AgO$_2$N$_2$ coordination about Ag is completed by bonds to the hetero nitrogens of two different substituted 2-ap molecules, one in a unidentate mode (molecule B) [Ag(1)−N(1B), 2.267(4) Å] the other in a bidentate bridging mode (molecule A), [Ag(1)−N(1A), 2.268(4) Å]. Bond angles about the silver range from 101.8 to 125.7(1)° (mean, 109.1°). This second pyrimidine molecule has 2-fold rotational symmetry coincident with crystallographic symmetry and links the cyclamer repeating units into a network polymer structure (Figure 7). Structural stability in this compound is also enhanced by two hydrogen-bonding interactions involving the 2-amino substituent group of molecule B. The first of these is a linear intramolecular association with a ring sulfonate oxygen [N(21B)−H(21A)- - -O(13A), 2.912(4) Å, N−H- - -O, 179(3)°]; the second, an intermolecular association with an inversion-related B molecule [N(21B)−H(21B)- - -N(3B), 3.006(4) Å, N−H- - -N, 170(3)°]. This

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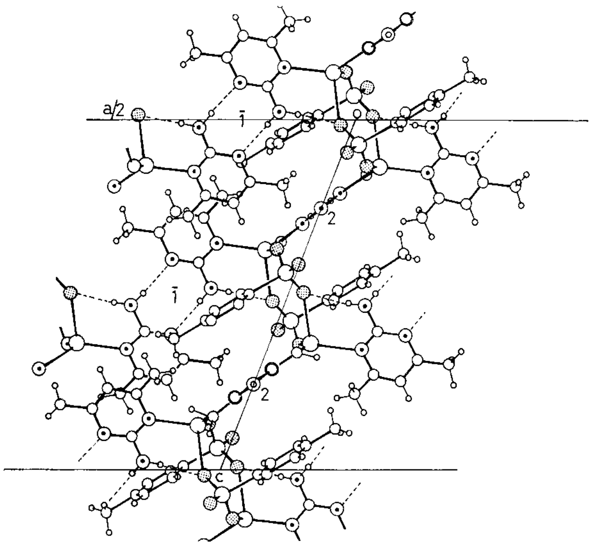

Figure 7. Packing of **5** in the unit cell viewed down *b*, showing the hydrogen-bonding interactions.

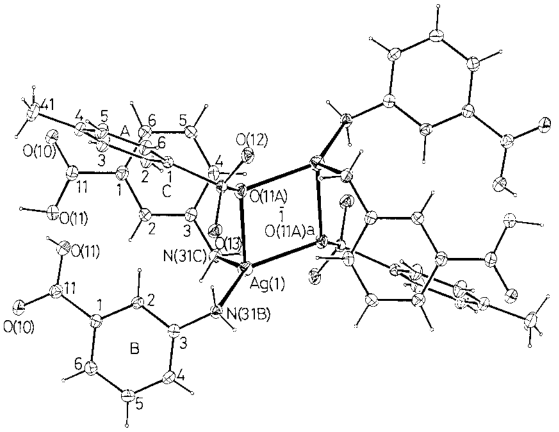

Figure 8. Atom-numbering scheme and molecular structure for the complex dimer [{Ag(pts)}$_2$(3-aba)$_4$] (**6**).

results in a cyclic hydrogen-bonded ring [graph set $R^2_2(8)$[15]], similar to that found in the structure of the parent 2-aminopyrimidine[16] (comparative distance 3.072 Å), and in a number of molecular adducts of 2-aminopyrimidine with carboxylic acids.[17]

[{Ag(pts)}$_2$(3-aba)$_4$] (6). The 1:2 adduct of Ag(pts) with 3-aminobenzoic acid, [{Ag(pts)}$_2$ (3-aba)$_4$] (**6**), is similar to compound **3** of this series, comprising discrete nonbridged centrosymmetric dimers (Figure 8). These have distorted tetrahedral four-coordinate AgO_2N_2 centers bridged by asymmetric bis bridges via the O(11A) sulfonate oxygens [Ag(1)−O(11A), 2.441(2) Å; Ag(1)−O(11A)^a, 2.627(2) Å (a = $-x$, $-y$, $-z$)] and to two amine nitrogens of the two independent 3-aba molecules [Ag(1)−N(31B), 2.238(3) Å; Ag(1)−N(31C), 2.285(3) Å]. The Ag- - -Ag separation in the dimer is 3.809(1) Å. Angles about the distorted tetrahedral silver center range from 82.7 to 134.7(2)° [mean, 107.3°], while the bridge angle at O(11A) is 97.4(3)°. The other two sulfonate oxygens are associated with the amine groups of both 3-aba adduct molecules in both intramolecular hydrogen bonds [O(13A)- - -H(32B)−N(31B), 2.898(4) Å, O- - -H−N, 169(3)°; O(12A)- - -H(32C)-N(31C), 3.039(4) Å, O- - -H−N, 146(3)°] and intermolecular hydrogen bonds [O(13A)- - -H(31B)−N(31B), 2.969(4) Å, O- - -H−N, 137(3)°; O(12A)- - -H(31C)−N(31C), 2.993(4) Å, O- - -H−N, 140(3)°]. The carboxylic acid groups on the 3-aba molecules also form intermolecular hydrogen-bonding relationships with other carboxylic acid groups [O(11B)−H(11B)- - -O(10C), 2.648(4) Å, O−H- - -O, 176(3)°; O(11C)−H(11C)- - -O(10B), 2.636(4) Å, O- - -H−O, 159(3)°], giving cyclic units [graph set $R^2_2(8)$] similar to those found in the solid-state structures of most carboxylic acids.[18] These link the complex molecular dimers along the *b* cell direction (Figure 9).

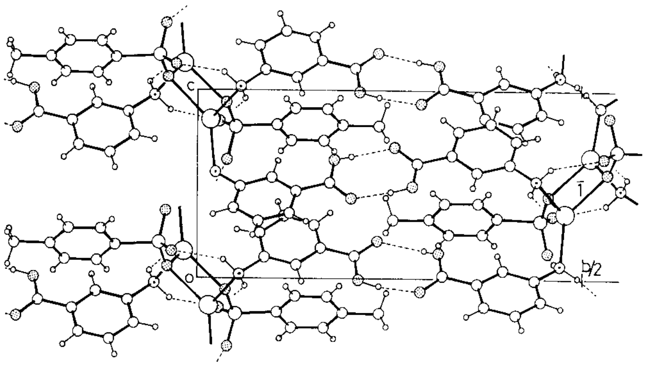

Figure 9. Packing of **6** in the unit cell viewed down *a*, showing the hydrogen-bonding interactions.

[{Ag(pts)}(an)$_3$] (7). The 1:3 complex adduct formed between *p*-toluenesulfonate and aniline, [{Ag(pts)}(an)$_3$] (**7**), as indicated from analytical data (C, H, N analyses and infrared spectroscopy), represents not only an unusual stoichiometry but also a rare example of an unstable compound for this series. Because aniline has no secondary associative groups to enhance crystal stabilization, formation of the basic polymer structure such as found with the 1:1 pyridine adduct (**2**) might be expected. This type of structure readily forms via insertion of the donor group (or groups) (the pyridine molecules) in the tetrahedral silver coordination sphere. Infrared spectroscopy indicates that the aniline molecules in **7** are present in both coordinated and adducted states, with a structure probably of the type [Ag(pts)}(an)$_2$]·an. Amine coordination should result in the appearance of a strong band in the 1100−1200 cm^{-1} region due to the $-NH_2$ wagging vibration,[19] but in this region there is considerable interference due to the presence of the ν-(S−O) absorptions. However, similar aniline clathrates of the type [M^{II}(NH$_3$)$_2$][Ni(CN)$_4$]·2an (M = Ni, Cu, Zn, Cd) have previously been reported.[20] Further evidence that this is the case with compound **7** is found in the rapid loss of diffracting power of the crystal in air without any visible morphological change, indicating loss of the adducted aniline.

Infrared Spectroscopy. The infrared spectrum of the parent compound silver(I) *p*-toluenesulfonate shows, in addition to the well-resolved aromatic frequencies extending through the region 1000−500 cm^{-1}, those frequencies characteristic of the fundamental and split ν_3 S−O stretching modes in the range 1180−1000 cm^{-1}.[21] This is the case with **1** because of the presence

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of both bidentate and bridging sulfonate groups in the structure. With adduct formation, the combined characteristic frequencies for each species are expected in the spectrum, with little change since only coordination occurs and no major perturbation of the basic lattices results. This is apart from some relaxation in the S−O frequencies with change in the coordination mode and some rearrangement in certain members due to the generation of a hydrogen-bonding network. This may be seen in the spectrum of the pyridine adduct (**2**), where no appreciable changes in the high-frequency region due to coordinated pyridine are expected[22] [cf. those due to in-plane and out-of-plane ring deformations (at ca. 600 and 400 cm^{-1} shifting to ca. 620 and 420 cm^{-1} respectively)]; the only change is the slight increase in the ν(S−O) frequencies by ca. 5−20 cm^{-1}. No hydrogen-bonding effects are expected because of the absence of these in either the parent or in **2**. A similar situation is expected with the 2-aminopyridine adduct **3**, where coordination is through the hetero N and whose spectrum is analogous to the previously reported spectra for the adducts of 2-(methylamino)pyridine with $AgClO_4$ and $AgNO_3$, although with 2-aminopyridine, the coordination appeared to be through the amino N.[23] This is the case with the *m*-aminobenzoic acid complex (**6**) where coordination is through the amino N and occurs with considerable hydrogen-bonding interaction through both amino N and carboxylic acid groups. With both **3** and **6**, a general sharpening of the NH stretching frequencies indicates an increase in the rigidity due to these hydrogen-bonding systems, correlating with the observation from the crystal structure determinations, while with **7**, as discussed previously, the effect is similar to that found for compound **6**.

Conclusions

Complex adducts of silver(I) *p*-toluenesulfonate with aromatic nitrogen Lewis bases, of the type [Ag(pts)(L)], are readily formed and give mostly air-stable crystals which lend themselves to characterization using X-ray diffraction methods. With these, the basic Ag(pts) complex is retained with the N donor or donors inserting in the coordination sphere of silver, but with considerable rearrangement of the lattice. Both dimeric and polymeric structures result, with stabilization enhanced by hydrogen bonding through secondary interactive groups. Considering the complexity and structural diversity of the compounds reported in this work, infrared spectroscopy may be considered at best an indicator of complex formation to be used in conjunction with other simple physical tests (density; solubility in nonaqueous solvents, e.g., $CHCl_3$) as indicators of complex formation. Further work is continuing with this adduct series involving particularly the aliphatic amine adducts, where it may be anticipated that lattice stability will not be as great as those considered here. To date, one example, the adduct with urea, $[\{Ag(pts)\}_2(urea)_2]_n$, has been synthesized and characterized by X-ray methods[24] and is a ribbon polymer based on a urea-*N*,*O*-bridged cyclic dimer in which the silver centers have trigonal bipyramidal $AgNO_4$ stereochemistry.

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Supporting Information Available: Six X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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