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Preparation and Crystal Structure of the Silver(I) *p*-Toluenesulfonate−*p*-Aminobenzoic Acid Complex Polymer Adduct, the First Reported Example of a Silver(I) Complex Involving Two Different Organic Acid Species

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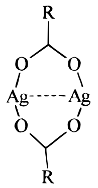
The complexes of silver(I) with carboxylic acids represent a group of metal compounds which, despite their usage in synthetic organic chemistry [e.g., the Hunsdiecker reaction (decarboxylation), the Simonini reaction (ester synthesis), and the Prévost reaction (diol synthesis)],[1] until recently had few structurally characterized examples.[2] Of the currently known silver(I) carboxylates, the majority are based on a bis(carboxylato-*O,O′*)-bridged dimer (**I**), which may be discrete [e.g., silver(I) benzoate[3] or silver(I) salicylate (polymorph 1)[4]] or extended in one or more of the axial sites of the dimer into tetramer or polymer variations (**II**) [e.g., silver(I) phenoxyacetate].[5] These variations have been classified in a number of works.[6] Very few examples are known in which a linear two-coordinate stereochemistry about silver is found (**III**) [e.g., silver(I) (4-chloro-2-methylphenoxy)acetate].[7] With the analogous silver(I) sulfonates, although few structures are known, all are polymeric, silver involving most sulfonate oxygens in variable coordination modes.[8] As an extension of our work on the structural characterization of the silver(I) carboxylates, the structure determination of a mixed sulfonate−carboxylate was attempted in order to assess the effect of an interactive substituent group on the formation of molecular systems having potential for specialist optical properties. The isomeric aminobenzoic acids were chosen initially because of their known ability to form extended hydrogen-bonded systems (often involving proton transfer), *via* both the interactive carboxylic acid and the amine ring substituent.[9] The first of these silver compounds, isolated as the only product from refluxing stoichiometric quantities of silver(I) *p*-toluenesulfonate and *p*-aminobenzoic acid in ethanol,[10] *catena*-(μ-4-aminobenzoic acid)(μ-4-toluenesulfonato-*O,O′,O″*)silver(I), is reported here. The crystal structure determination[11] has shown a two-dimensional sheet structure based upon a distorted tetrahedral



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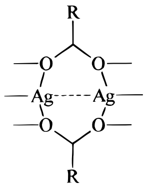

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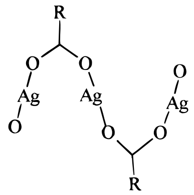

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(10) Preparation: The complex was prepared by refluxing 1:1 stoichiometric quantities of silver(I) *p*-toluenesulfonate (0.56 g, 2 mmol) and *p*-aminobenzoic acid (0.27 g, 2 mmol) in ethanol ($30 cm^3$) for 10 min. Care was taken to exclude only natural light during the preparation. The white solid which precipitated from this solution was removed and redissolved in methanol, and the solution was allowed to partially evaporate at room temperature in the dark. Colorless needle crystals formed in *ca.* 60% yield after several days of standing at room temperature. These crystals are relatively stable both chemically and photochemically. The infrared spectrum and elemental analysis (C, H, N) indicated the presence of coordinated silver, *p*-aminobenzoic acid, and *p*-toluenesulfonate in the ratio 1:1:1. Anal. Calc for $C_{14}H_{14}AgNO_5S$: C, 40.4; H, 3.4; N, 3.4. Found: C, 40.5; N, 3.4; N, 3.7.

(11) (a) Crystal data: $C_{14}H_{14}AgNO_5S$, $M_r = 416.2$, monoclinic, space group *C2/c*; $a = 35.86(2)$, $b = 8.958(4)$, $c = 9.695(5)$ Å; $\beta = 109.65(2)°$; $V = 2933(3)$ Å^3; $Z = 8$; $D_c = 1.885$, $D_m = 1.90$ g cm^{-3}; $F(000) = 1664$; μ(Mo Kα) = 15.4 cm^{-1}; $T = 293(2)$ K. (b) Data collection and structure solution and refinement: Data were collected on an Enraf-Nonius CAD-4 diffractometer (monochromatic Mo Kα radiation, $\lambda = 0.710\,73$ Å) from a cleaved specimen (0.25 × 0.14 × 0.12 mm). Of 2717 reflections collected up to $2\theta_{max} = 54.3°$ in the ranges $h = 0-42$, $k = 0-10$, and $l = -11$ to $+11$, 2672 were unique ($R_{int} = 0.045$; maximum intensity decay *ca.* 1.5%). Data were corrected for absorption using semiempirical methods[12] The structure was solved by Patterson methods (SHELXS-86[13]) and refined (on F^2), with all non-hydrogen atoms anisotropic (SHELXL-93[14]). Hydrogens were included at calculated positions and their positional parameters refined and their isotropic thermal values fixed. Final residuals R1 $[=\sum\{|F_o| - |F_c||/|F_o|\}]$ and wR2 $[=\{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)\}^{1/2}]$ {with $w = \sigma^2(F_o^2) + (0.0656P)^2 + 3.84P$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$}, and *S* were 0.032, 0.086, and 1.01, respectively, for 2218 reflections with $F_o > 4.0\sigma(F_o)$. The maximum peak in the final difference map was 0.86 e Å^{-3} (adjacent to Ag).

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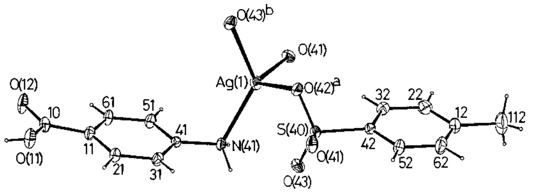

Figure 1. Molecular structure and atom numbering scheme for the repeating unit in the complex polymer, showing 20% probability ellipsoids. Unless otherwise indicated, atoms are carbon. Selected bond distances (Å) and angles (deg): Ag(1)−N(41), 2.223(3); Ag(1)−O(41), 2.518(3); Ag(1)−O(42)^a, 2.309(3); Ag(1)−O(43)^b, 2.468(3); N(41)−Ag(1)−O(41), 132.0(1); N(41)−Ag(1)−O(42)^a, 112.3(1); N(41)−Ag(1)−O(43)^b, 128.0(1); O(41)−Ag(1)−O(42)^a, 94.57(9); O(41)−Ag(1)−O(43)^b, 95.9(1); O(42)^a−Ag(1)−O(43)^b, 76.21(9). a = x, 1 − y, −$^1/_2$ + z; b = $^1/_2$ − x, $^1/_2$ − y, z.

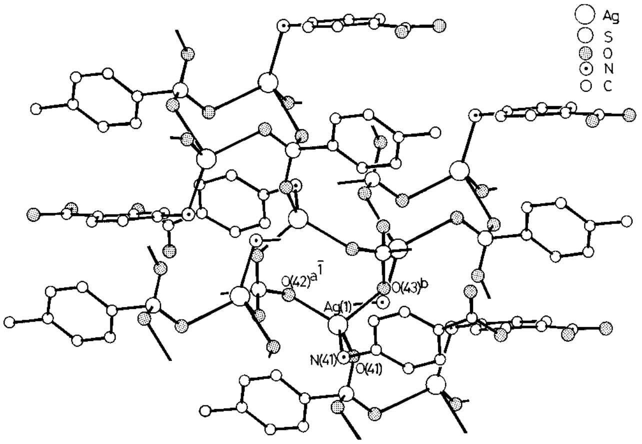

Figure 2. Two-dimensional structure of the complex polymer viewed down the approximate *b* cell direction (down the sheet edge). Hydrogens are omitted for clarity.

AgO_3N center involving three oxygens from independent sulfonate residues [Ag−O = 2.309, 2.468, 2.518(3) Å] and an amine nitrogen [Ag−N = 2.223(3) Å] (Figures 1 and 2). The bond angle range for the coordination sphere is 76.21(9)−132.0(1)°. This system is very different from the structures generally observed for the silver(I) carboxylates, including silver(I) *p*-aminobenzoate,[15] a conventional bis(carboxylate)-bridged dimer, extended into a polymer *via* Ag−N bonds through the amine substituent. In the present structure, *p*-aminobenzoic acid behaves as a Lewis base adduct of silver(I) *p*-toluenesulfonate, which, although its structure has not been reported, would be assumed to be a three-dimensional polymer similar to the known silver(I) sulfonates,[8] having significant oxygen involvement in coordination to silver. In the present example, the amino group of the *p*-aminobenzoic acid adduct molecule (which is similar to the two crystalline polymorphs of the parent acid in being non-zwitterionic)[16] acts as the donor group essentially in the manner of the Lewis base adducts of the silver(I) halides.[17] Although examples of this type of interaction are relatively common, only one Lewis base adduct of a silver carboxylate is known, the silver(I) benzoate−pyridine adduct.[18] In addition, an unusual feature of the solid-state intermolecular associations for this compound is the absence of any hydrogen-bonding interactions involving the uncoordinated carboxylic group. This is usually an integral part of the packing modes of both homogeneous and heterogeneous acid pairs in the structures of these acids and their cocrystals. Hydrogen-bonding associations are found between the amine protons and adjacent sulfonate oxygens [N(41)−H(42)---O(43)^i = 3.111(2) Å, O−H---O = 165°, i = $^1/_2$ − x, $^1/_2$ + y, $^1/_2$ − z; N(41)−H(43)---O(43)^{ii} = 3.069(2) Å, N−H---O = 118°, ii = x, 1 − y, −$^1/_2$ + z; N(41)−H(43)---O(42)^{iii} = 3.177(2) Å, N−H---O = 165°, iii = $^1/_2$ − x, $^3/_2$ − y, −z].

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Supporting Information Available: Tables of crystal data, atomic positional parameters, bond lengths and angles, anisotropic thermal displacement parameters, and hydrogen atom coordinates (6 pages). Ordering information is given on any current masthead page.

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