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Layered Coordination Polymer of Silver Methanesulfonate with 2,3,5,6-Tetramethylpyrazine

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Abstract—The complex $[Ag_2(Me_4\text{-}Pyz)(CH_3SO_3)_2] \cdot 2H_2O$ is synthesized, and its structure is determined. The crystals are monoclinic, space group $P2_1/n$, $a = 11.821(1)$, $b = 4.906(1)$, $c = 15.782(1)$ Å, $\beta = 94.34(1)°$, $V = 912.5(2)$ Å^3, ρ(calcd) = 2.104 g/cm^3, $Z = 2$. The Ag^+ ion is coordinated at the vertices of the distorted tetrahedron by the nitrogen atom of tetramethylpyrazine and three oxygen atoms of two methanesulfonate ions (Ag(1)–N(1) 2.283(2), Ag(1)–O(RSO_3^-) 2.386(3)–2.451(2) Å, angles at the Ag atom 86.8(1)°–129.1(1)°). The structure contains layers of sulfonate–silver chains and tetramethylpyrazine molecules extended along the direction [101].

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INTRODUCTION

Layered materials, most frequently metal phosphonates, are usually used to study the intercalation of guest molecules [1]. Sulfonate anions RSO_3^- are structurally analogous to phosphonate anions RPO_3^{2-}, but are weaker coordinating ligands than the latter. Sulfonate ions excel PF_6^- and ClO_4^-, in the ability to form coordination bonds with metals but are inferior to the NO_3^- and CF_3COO^- ions. As compared to those with phosphonates, coordination compounds with sulfonates are studied insufficiently.

Coordination compounds with the RSO_3^- ions, where R = CF_3, XC_6H_4 (X = H, CH_3, NH_2), are studied most frequently [2, 3].

Silver sulfonates are classified as the so-called "inorganic–organic" layered solid materials [4, 5]. The inorganic part is the –Ag–OSO–Ag– polymer, and the R(RSO_3^-) radicals directed at the both sides of the sulfonatosilver layer serve as the organic part. In methanesulfonate $Ag(CH_3SO_3)$, the silver atom has a distorted trigonal bipyramidal coordination with three short (2.34–2.43 Å) and two long (2.63 Å) Ag–O bonds [6].

It is shown that the $Ag(CF_3SO_3)(C_2H_5OH)_{0.5}$ structure contains layers of silver trifluoromethanesulfonates and ethanol molecules with two crystallographically independent Ag^+ centers (coordination number of Ag(1) and Ag(2) are five and six, respectively). The Et and CF_3 groups are directed to the interlayer space [2].

Silver benzene sulfonate $Ag(C_6H_5SO_3)$ contain two-dimensional networks including only the Ag, S, and O atoms with the hexacoordinated Ag^+ centers. The phenyl groups are arranged at the both sides of the layers in the interlayer space [4]. The layered structure of silver *p*-toluenesulfonate $Ag(CH_3C_6H_5SO_3)$include analogous two-dimensional networks with the pentacoordinated centers Ag^+ [7].

The design and construction of mixed-ligand coordination polymers are of considerable interest in the recent years due to their potential use in catalysis, adsorption, host–guest chemistry, and electrofunctional materials [8, 9]. It seems interesting to modify the sulfonate complexes by various N-containing ligands because of their ability to create unusual structures with important properties.

In the coordination of silver sulfonates with N-containing organic ligands, the sulfonate ion can be a counterion compensating the cation charge or a coordinating ligand [10].

The purpose of the present work is to synthesize the coordination polymer based on silver methanesulfonate and tetramethylpyrazine $[Ag_2(Me_4\text{-}Pyz)(CH_3SO_3)_2] \cdot 2H_2O$ (**I**) and to study its structure.

EXPERIMENTAL

Synthesis. The starting reactants in the synthesis of compound **I** were $Ag(CH_3SO_3)$ (Aldrich) and 2,3,5,6-Me_4Pyz (high-purity grade) taken in a ratio of 1 : 2.5. A weighed sample of $Ag(CH_3SO_3)$ (0.203 g) was dissolved in isopropyl alcohol (10 ml) with the addition of

Table 1. Selected crystallographic data and experimental characteristics for structure **I**

Parameter	Value
FW	578.16
Crystal sizes, mm	$0.35 \times 0.20 \times 0.20$
Crystal system	Monoclinic
Space group	$P2_1/n$
Cell parameters:	
a, Å	11.821(1)
b, Å	4.906(1)
c, Å	15.782(1)
β, deg	94.34(1)
V, Å^3	912.5(2)
Z	2
ρ_{calcd}, g/cm	1.759
μ_{Mo}, mm^{-1}	1.246
F(000)	504
Temperature, K	293
Radiation (λ, Å)	MoK_α (0.71073), graphite monochromator
Scan mode	ω
θ range, deg	2.08–29.97
Index range	$-1 \le h \le 16$, $-1 \le k \le 6$, $-22 \le l \le 22$
Total number of reflections/number of independent reflections	3627/2649 (R_{int} = 0.0213)
Number of reflections with $I \ge 2\sigma(I)$	1942
Number of refined reflections	110
GOOF for F^2	0.910
R ($I \ge 2\sigma(I)$)	R_1 = 0.0317, wR_2 = 0.1006
R (all data)	R_1 = 0.0550, wR_2 = 0.1169
Extinction coefficient	0.012(2)
Residual electron density (max/min), e Å^{-3}	0.703/–1.082

2–3 droplets of distilled water. Tetramethylpyrazine (Me_4Pyz) (0.340 g) was also dissolved in isopropanol (10 ml). Then the solutions were poured together at room temperature and placed in dark. After several days, crystals were formed, separated from the mother liquor, dried in air, and studied by elemental analysis, IR spectroscopy, and X-ray diffraction analysis. The yield of the product was 70%.

Found (%): C 21.58; N 4.72; S 11.66; H 3.41.
For $C_{10}H_{22}N_2O_8S_2Ag_2$
Anal. calcd. (%): C 20.76; N 4.84; S 11.07; H 3.81.

IR spectra were recorded on a Nexus Fourier spectrometer (Nicolet) in the interval from 400 to 4000 cm^{-1} (KBr pellets).

X-ray diffraction analysis. The experimental material for crystals **I** was obtained on an Enraf-Nonius CAD4 automated diffractometer. The structure was solved by a direct method and refined by the least-squares method in the full-matrix anisotropic approximation for all non-hydrogen atoms. Positions of hydrogen atoms were calculated geometrically and included into refinement by the riding model with fixed isotropic temperature parameters. The hydrogen atoms of the water molecules were found from the difference Fourier synthesis. All calculations were performed using the SHELXL-97 programs.

Selected characteristics of experiment and the unit cell parameters are given in Table 1. The crystallographic data were deposited with the Cambridge Crystallographic Data Centre (no. 729906; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The IR spectrum of compound **I** contains absorption bands characteristic of vibrations of coordinated Me_4Pyz (486, 1026, 1223, 1410, 1447, and 2930–3011 cm^{-1}) and absorption bands of bending and stretching vibrations of the water molecules (1630 and 3436 cm^{-1}, respectively). The spectrum also exhibits absorption bands ν(S–O) of the methanesulfonate anion at 1059 and 1195 cm^{-1}, indicating the coordination of the latter with metal.

Infinite ribbons consisting of the Ag atoms and bridging CH_3SO_3 groups extended along the y axis are formed in structure **I** by the interaction of the sulfonate ions with the Ag atoms (Fig. 1). The thickness of the sulfonatosilver ribbon-"plate" is 3.58(3) Å. The Ag^+ ion is coordinated at the vertices of the distorted tetrahedron by the nitrogen atom of tetramethylpyrazine and three oxygen atoms of three bridging methanesulfonate ions (Ag(1)–N(1) 2.283(2); Ag(1)–O(RSO_3^-) 2.386(3), 2.396(3), and 2.451(2) Å; angles at the Ag atom

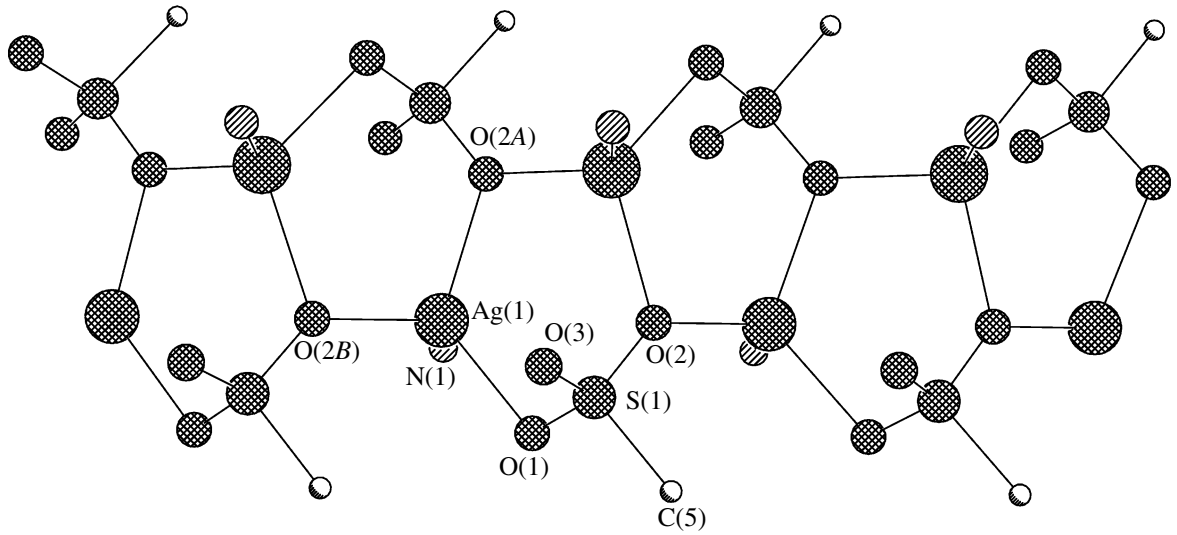

Fig. 1. Fragment of the structure of the infinite sulfonatosilver ribbons (symmetry transformations of atoms: O(2*A*) $1^1/_2 - x$, $1^1/_2 + y$, $1^1/_2 - z$; O(2*B*) x, $1 + y$, z).

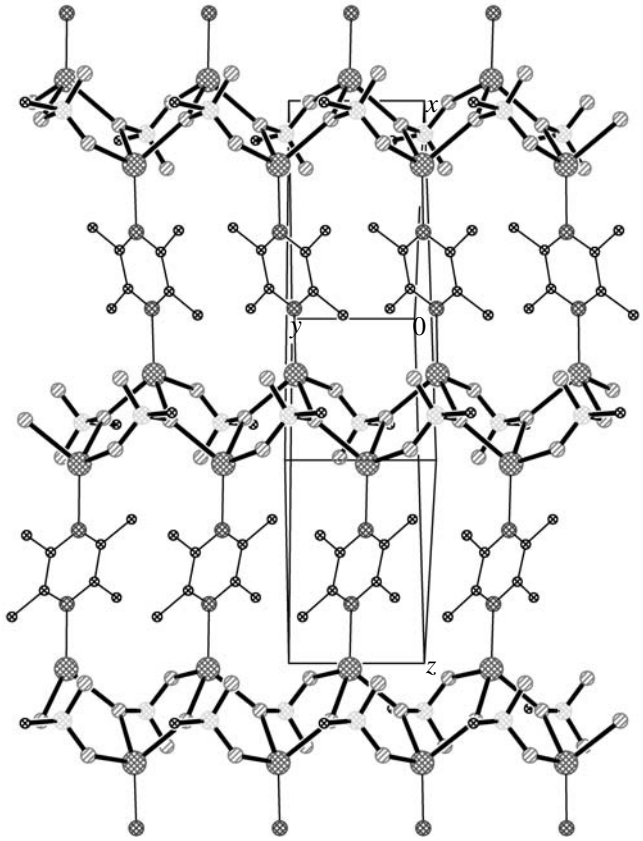

Fig. 2. Layer of the sulfonatosilver ribbons and tetramethylpyrazine molecules along [101].

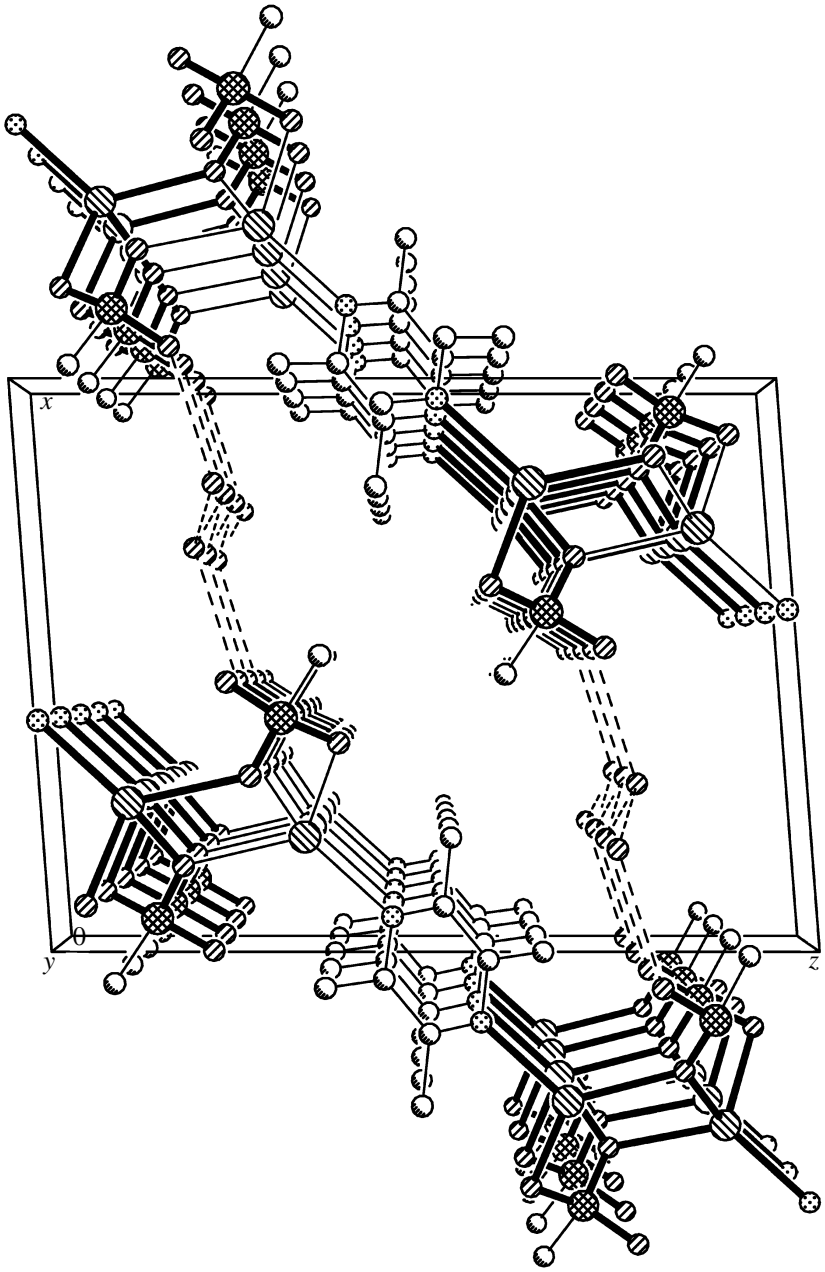

Fig. 3. General view of structure **I** along [010].

86.8(1)°–129.1(1)°). The μ^3-bridging ligands CH_3SO_3 bind three silver atoms. Two crystallographically equivalent O(2) atoms, the O(1) atom, and the terminal O(3) atom participate in the coordination of Ag.

Layers are formed along the direction [101] due to the interaction of silver methanesulfonate with tetramethylpyrazine molecules (Fig. 2). The methyl groups of sulfonate and tetramethylpyrazine and the water molecules are localized in the interlayer space. The distance between the layers is 9.97 Å. The water molecules form hydrogen bonds O(*w*)–H···O(SO_3) with the terminal oxygen atoms of the sulfonate ions and O atoms of the adjacent water molecules O(*w*)–H···O(*w*)' 2.777(7) Å (Table 2, Fig. 3). As a result, clusters are formed of water molecules as zigzag supramolecular chains extended along the *x* axis (Fig. 4). The water molecules

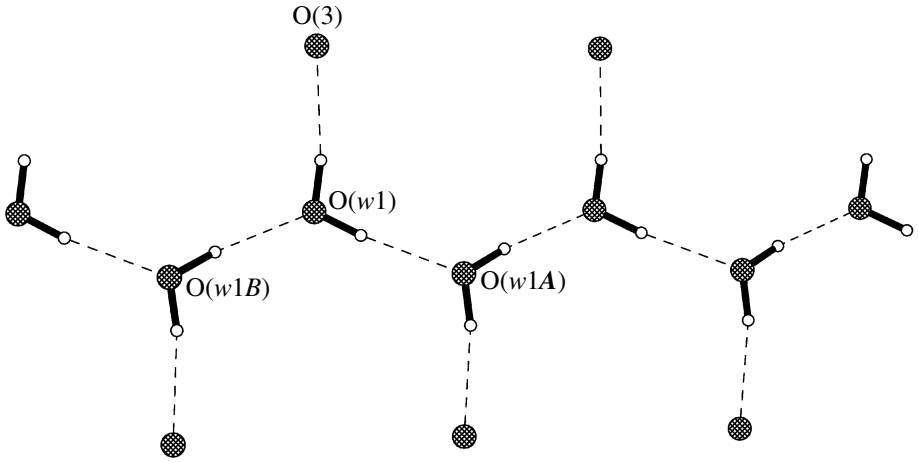

Fig. 4. Supramolecular zigzag chains of water molecules (symmetry transformations of atoms: O(*w*1*A*) $2^1/_2 - x$, 1/2 + *y*, $1^1/_2 - z$; O(*w*1*B*) $2^1/_2 - x$, –1/2 + *y*, $1^1/_2 - z$).

are both proton donors and acceptors, and the noncoordinated sulfonate O atoms act only as proton acceptors (Table 2).

The formation of clusters of H_2O molecules in silver sulfonates is a rather rare phenomenon, which was first found in $[Ag(L^1)(Pyz)] \cdot H_2O$ (**II**) (L^1 is naphthalenesulfonate, $C_{10}H_7SO_3$; Pyz = $N_2C_4H_4$). The clusters look like spiral chains with an O(*w*)···O(*w*)' distance of 2.685(5) Å [10]. Note that the O(*w*)···O(*w*)' distances in the structure of usual ice, in liquid water, and in water vapor are 2.74, 2.85, and 2.98 Å, respectively [9].

An H_2O molecule has two protons and two lone electron pairs, which can result in both tetrahedral and trigonal coordination. In the studied structure **I** and in compound **II**, the water molecule has a trigonal configuration.

It is important to mention the role of such a ditopic ligand as (Me_4Pyz) in the formation of layers in structure **I** due to organometallic bonds –Ag–N(Me_4Pyz)N–Ag– and the role of water in the stabilization and formation of the 3D supramolecular structure.

The analysis of our results and published data shows that the layered motif is retained even in the presence of an equivalent amount of secondary N-containing ligands in the structure in spite of the low coordination ability of sulfonate anions. However, due to the higher coordination ability of the latter, the sulfonate ions in the coordination sphere of Ag^+ are replaced by the secondary ligand. This substitution results in substantial structural changes, when the number of coordinated oxygen atoms of the RSO_3^- groups decreases down to their complete displacement from the coordination sphere of silver.

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Table 2. Hydrogen bonding geometry in structure **I**

Contact A–H···B	Distance, Å			Angle AHB, deg	Coordinates of B atom
	A···B	A–H	H···B		
O(*w*1)–H(1)···O(3)	2.814(7)	0.89	1.94	169	*x*, *y*, *z*
O(*w*1)–H(2)···O(*w*1*A*)	2.777(7)	0.92	1.86	170	$2^1/_2 - x$, 1/2 + *y*, $1^1/_2 - z$

research "Development of Methods for Synthesis of Chemical Substances and Creation of New Materials").

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