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Coordination Polymer of Ag Trifluoroacetate with 2-Methylpyrazine: Synthesis and Structure of $[Ag(CF_3CO_2)(2\text{-Me-Pyz})]$

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Abstract—The $[Ag(CF_3CO_2)(2\text{-Me-Pyz})]$ complex (where 2-Me-Pyz is 2-methylpyrazine) was synthesized and its structure was determined. The crystals are monoclinic, space group $P2_1/n$, a = 12.440(2) Å, b = 2.605(3) Å, c = 12.646(3) Å, β = 95.95(3)°, V = 1972.3(7) Å^3, ρ = 2.122 g/cm^3, Z = 8. The structure consists of the polymer zigzag chains of $[Ag(C_5H_6N_2)]^-_\infty$ united into a three-dimensional framework through $(CF_3CO_2)^-$ anions.

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The authors of [1, 2] suggested that coordination polymers and supramolecular compounds could be synthesized from so-called secondary building units (SBU). By making use of such a building unit, i.e., silver triacetate dimer, $Ag_2(CF_3CO_2)_2$, and pyrazine and tetramethylpyrazine, the coordination polymers of the composition $[Ag(CF_3CO_2)\,L]$ were synthesized (where L is pyrazine and tetramethylpyrazine). In these compounds, pairs of Ag^+ ions are connected by carboxylate bridges. In addition, the Ag^+ ions coordinate neutral N-containing ditopic ligands to give layered structures [3].

This work was devoted to the synthesis of $[Ag(CF_3CO_2)(2\text{-Me-Pyz})]$ (**I**) (where 2-Me-Pyz is 2-methylpyrazine, $C_5H_6N_2$), and X-ray diffraction study of its structure.

EXPERIMENTAL

Synthesis of $[Ag(CF_3CO_2)(2\text{-Me-Pyz})]$. Solutions of $Ag(CF_3CO_2)$ and 2-Me-Pyz were prepared in isopropyl alcohol. The reaction was performed at the reagent molar ratio of 1 : 1, i.e., $Ag(CF_3CO_2)$ (0.22 g, 1 mmol) and 2-Me-Pyz (0.094 g, 1 mmol). The reaction mixture was stored in the dark, and in three weeks, rhomboid crystals of **I** were formed. The crystals were studied by the elemental analysis, IR and X-ray diffraction methods.

For $[Ag(CF_3CO_2)(C_5H_6N_2)]$				
anal. calcd. (%):	Ag 34.28,	N 8.89,	C 26.67,	H 1.90.
Found (%):	Ag 33.60,	N 8.00,	C 28.90,	H 2.50.

IR spectra of the complex were recorded on a Nexus Fourier spectrometer at 200–4000 cm^{-1} with samples prepared as mineral oil mulls. IR spectrum of complex **I** contains absorption bands characteristic of the $CF_3CO_2^-$ anion (1023, 1603, and 1745 cm^{-1}) and 2-Me-Pyz (650, 1010, 1230, and 1580 cm^{-1}).

The study of the thermal stability of the complex showed that at 130°C, 29.3% of its mass is lost due to removal of methylpyrazine molecule. The complete destruction of the complex with the formation of Ag_2O occurs at 230°C.

X-ray diffraction analysis was performed on a CAD4 Enraf-Nonius diffractometer. Absorption correction was applied empirically by North–Philips algorithm, by making use of two Ψ-scan curves. The structure was solved by the heavy-atom method and refined by full-matrix least-squares method for all non-hydrogen atoms. The obtained abnormally high values of thermal parameter for the F atoms of both independent $CF_3CO_2^-$ ions suggest their sufficiently high degree of disordering, which does not allow determination of possible orientations of the F atoms. The H atoms were localized from geometrical analysis and included in refinement in the rider model with isotropic thermal parameters (for all H atoms, U_{eq} = 0.08 Å^2). All calculations were carried out with SHELXS86 and SHELXL93 programs.

Crystallographic parameters and summary of data collection for structure **I** are listed in Table 1; coordinates of atoms and their thermal parameters are given in Table 2, selected bond lengths and bond angles are presented in Table 3.

Table 1. Crystallographic parameters and summary of data collection for structure **I**

Empirical formula	$C_7H_6AgF_3N_2O_2$
M	315.01
Crystal size, mm	$0.25 \times 0.23 \times 0.18$
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell parameters:	
a, Å	12.440(2)
b, Å	12.605(3)
c, Å	12.646(3)
β, deg	95.95(3)
V, Å^3	1972.3(7)
Z	8
ρ(calcd.), g/cm^3	2.122
μ_{Mo}, mm^{-1}	2.070
F(000)	1216
Temperature, K	293
Radiation (λ, Å)	MoK_α(0.71073)
Scan type	ω/θ
Range of θ, deg	2.29–30.48
Range in indices	$-17 \le h \le 0$, $0 \le k \le 17$, $-27 \le l \le 18$
Total number of reflections	5201
Number of independent reflections	5009 (R_{int} = 0.0197)
Number of refined parameters	272
GOOF on F^2	0.723
R ($I > 2\sigma(I)$)	R_1 = 0.0445, wR_2 = 0.1445
Coefficient of extinction	0.0018(4)
Residual electron density (max/min), e/Å^3	1.374/–0.763

Table 2. Coordinates of atoms and their thermal parameters ($U_{eq} = 1/3\Sigma U_{ij}$) for structure **I**

Atom	x	y	z	U_{eq}, Å^2
Ag(1)	0.22947(4)	0.26170(4)	0.39532(4)	0.0430(2)
Ag(2)	0.10174(5)	0.25371(4)	0.77018(4)	0.0445(2)
O(1)	–0.0311(4)	0.2260(5)	0.6214(4)	0.056(1)
O(2)	0.1082(5)	0.2344(5)	0.5265(5)	0.063(2)
O(3)	0.3786(4)	0.2799(6)	0.5297(4)	0.065(2)
O(4)	–0.0281(5)	0.2227(6)	0.8909(4)	0.065(2)
N(1)	0.1825(5)	0.4144(4)	0.7599(4)	0.042(1)
N(2)	0.2283(5)	0.4155(4)	0.3016(4)	0.041(1)
N(3)	0.2004(5)	0.0991(4)	0.7616(5)	0.044(1)
N(4)	0.2516(4)	0.1009(4)	0.3140(5)	0.042(1)
C(1)	0.1813(6)	0.5936(5)	0.2601(6)	0.045(1)
C(2)	0.1700(5)	0.5017(5)	0.3178(5)	0.039(1)
C(3)	0.2976(6)	0.4241(5)	0.2273(6)	0.054(2)
C(4)	0.1937(6)	0.0162(5)	0.3304(6)	0.051(2)
C(5)	0.1709(5)	0.4981(5)	0.8223(6)	0.041(1)
C(6)	0.2288(6)	0.5889(5)	0.8098(6)	0.046(2)
C(7)	0.1866(7)	0.0144(6)	0.8202(6)	0.052(2)
C(8)	0.2460(7)	–0.0771(5)	0.8113(6)	0.054(2)
C(9)	0.0147(5)	0.2202(5)	0.5384(5)	0.039(1)
C(10)	–0.0381(5)	0.2122(6)	0.9867(5)	0.043(1)
C(11)	0.0927(8)	0.4896(7)	0.9039(8)	0.074(3)
C(12)	0.0933(8)	0.4959(7)	0.4006(8)	0.077(3)
C(9)'	–0.0610(7)	0.1908(9)	0.4409(7)	0.067(2)
C(10)'	0.0628(7)	0.1901(9)	1.0606(7)	0.068(2)
F(1)	–0.0246(9)	0.201(1)	0.3541(6)	0.209(6)
F(2)	–0.089(1)	0.096(1)	0.4351(9)	0.241(8)
F(3)	–0.1486(9)	0.232(2)	0.434(1)	0.29(1)
F(4)	0.0737(8)	0.250(1)	1.1410(8)	0.198(7)
F(5)	0.0622(8)	0.0971(9)	1.099(1)	0.222(7)
F(6)	0.1511(5)	0.197(1)	1.0194(7)	0.158(4)
H(1*A*)	0.139	0.655	0.274	
H(3*A*)	0.342	0.364	0.21	
H(4*A*)	0.143	0.020	0.383	
H(6*A*)	0.218	0.648	0.855	
H(7*A*)	0.134	0.017	0.870	
H(8*A*)	0.235	–0.137	0.857	
H(11*A*)	0.060	0.421	0.899	
H(11*B*)	0.130	0.499	0.974	
H(11*C*)	0.038	0.543	0.892	
H(12*A*)	0.097	0.426	0.430	
H(12*B*)	0.116	0.546	0.456	
H(12*C*)	0.020	0.512	0.372	

Table 3. Bond lengths and bond angles in structure **I***

Bond	*d*, Å	Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
Ag(1)–N(2)	2.271(5)	C(1)–C(2)	1.384(8)	N(4)Ag(1)O(3)	106.4(2)	N(4)C(4)C(3)$^{\#4}$	121.6(6)
Ag(1)–N(4)	2.302(5)	C(2)–C(12)	1.490(10)	O(2)Ag(1)O(3)	91.1(2)	N(1)C(5)C(6)	120.1(6)
Ag(1)–O(2)	2.380(5)	C(4)–C(3)$^{\#4}$	1.381(9)	N(1)Ag(2)N(3)	120.6(2)	N(1)C(5)C(11)	118.1(6)
Ag(1)–O(3)	2.394(6)	C(5)–C(6)	1.371(8)	N(1)Ag(2)O(4)	121.3(2)	C(6)C(5)C(11)	121.8(6)
Ag(2)–N(1)	2.270(5)	C(5)–C(11)	1.494(10)	N(3)Ag(2)O(4)	107.0(2)	N(3)$^{\#2}$C(6)C(5)	123.5(6)
Ag(2)–N(3)	2.311(5)	C(6)–N(3)$^{\#2}$	1.331(8)	N(1)Ag(2)O(1)	111.0(2)	N(3)C(7)C(8)	121.9(6)
Ag(2)–O(4)	2.368(5)	C(7)–C(8)	1.381(9)	N(3)Ag(2)O(1)	99.6(2)	N(1)$^{\#3}$C(8)C(7)	121.5(6)
Ag(2)–O(1)	2.398(6)	C(8)–N(1)$^{\#3}$	1.334(8)	O(4)Ag(2)O(1)	91.2(2)	O(2)C(9)O(1)	129.0(7)
O(1)–C(9)	1.247(7)	C(9)–C(9)'	1.518(10)	C(9)O(1)Ag(2)	109.3(4)	O(2)C(9)C(9)'	117.5(6)
O(2)–C(9)	1.202(8)	C(10)–C(10)'	1.511(11)	C(9)O(2)Ag(1)	143.2(5)	O(1)C(9)C(9)'	113.5(6)
O(3)–C(10)$^{\#1}$	1.223(8)	C(9)'–F(1)	1.237(11)	C(10)$^{\#1}$O(3)Ag(1)	108.8(4)	O(3)$^{\#6}$C(10)O(4)	127.1(7)
O(4)–C(10)	1.238(8)	C(9)'–F(3)	1.205(12)	C(10)O(4)Ag(2)	142.5(5)	O(3)$^{\#6}$C(10)C(10)'	115.3(6)
N(1)–C(8)$^{\#2}$	1.334(8)	C(9)'–F(2)	1.248(14)	C(8)$^{\#2}$N(1)C(5)	117.1(5)	O(4)C(10)C(10)'	117.6(6)
N(1)–C(5)	1.334(8)	F(4)–C(10)'	1.265(12)	C(8)$^{\#2}$N(1)Ag(2)	116.1(4)	F(1)C(9)'F(3)	107.5(12)
N(2)–C(3)	1.344(8)	F(5)–C(10)'	1.269(13)	C(5)N(1)Ag(2)	126.6(4)	F(1)C(9)'F(2)	100.0(12)
N(2)–C(2)	1.334(7)	F(6)–C(10)'	1.267(10)	C(3)N(2)C(2)	116.0(5)	F(3)C(9)'F(2)	99.9(13)
N(3)–C(6)$^{\#3}$	1.331(8)			C(3)N(2)Ag(1)	117.7(4)	F(1)C(9)'C(9)	116.2(8)
N(3)–C(7)	1.320(8)			C(2)N(2)Ag(1)	126.1(4)	F(3)C(9)'C(9)	115.7(9)
N(4)–C(4)	1.316(8)			C(6)$^{\#3}$N(3)C(7)	115.8(6)	F(2)C(9)'C(9)	115.3(9)
N(4)–C(1)$^{\#4}$	1.322(8)			C(6)$^{\#3}$N(3)Ag(2)	120.3(4)	F(6)C(10)'F(4)	105.3(11)
Angle	ω, deg	Angle	ω, deg	C(7)N(3)Ag(2)	123.7(4)	F(6)C(10)'F(5)	105.1(11)
N(2)Ag(1)N(4)	120.8(2)	N(2)C(2)C(1)	121.0(6)	C(4)N(4)C(1)$^{\#4}$	116.9(6)	F(4)C(10)'F(5)	104.7(11)
N(2)Ag(1)O(2)	121.1(2)	N(2)C(2)C(12)	117.8(6)	C(4)N(4)Ag(1)	123.4(4)	F(6)C(10)'C(10)	115.6(8)
N(4)Ag(1)O(2)	107.3(2)	C(1)C(2)C(12)	121.2(6)	C(1)$^{\#4}$N(4)Ag(1)	119.4(4)	F(4)C(10)'C(10)	113.5(8)
N(2)Ag(1)O(3)	104.5(2)	N(2)C(3)C(4)$^{\#5}$	121.9(6)	N(4)$^{\#5}$C(1)C(2)	122.5(6)	F(5)C(10)'C(10)	111.7(9)

* Symmetry transformations of atoms: $^{\#1}$ $x + 1/2, -y + 1/2, z - 1/2$, $^{\#2}$ $-x + 1/2, y + 1/2, -z + 3/2$; $^{\#3}$ $-x + 1/2, y - 1/2, -z + 3/2$, $^{\#4}$ $-x + 1/2, y - 1/2, -z + 1/2$, $^{\#5}$ $-x + 1/2, y + 1/2, -z + 1/2$, $^{\#6}$ $x - 1/2, -y + 1/2, z + 1/2$.

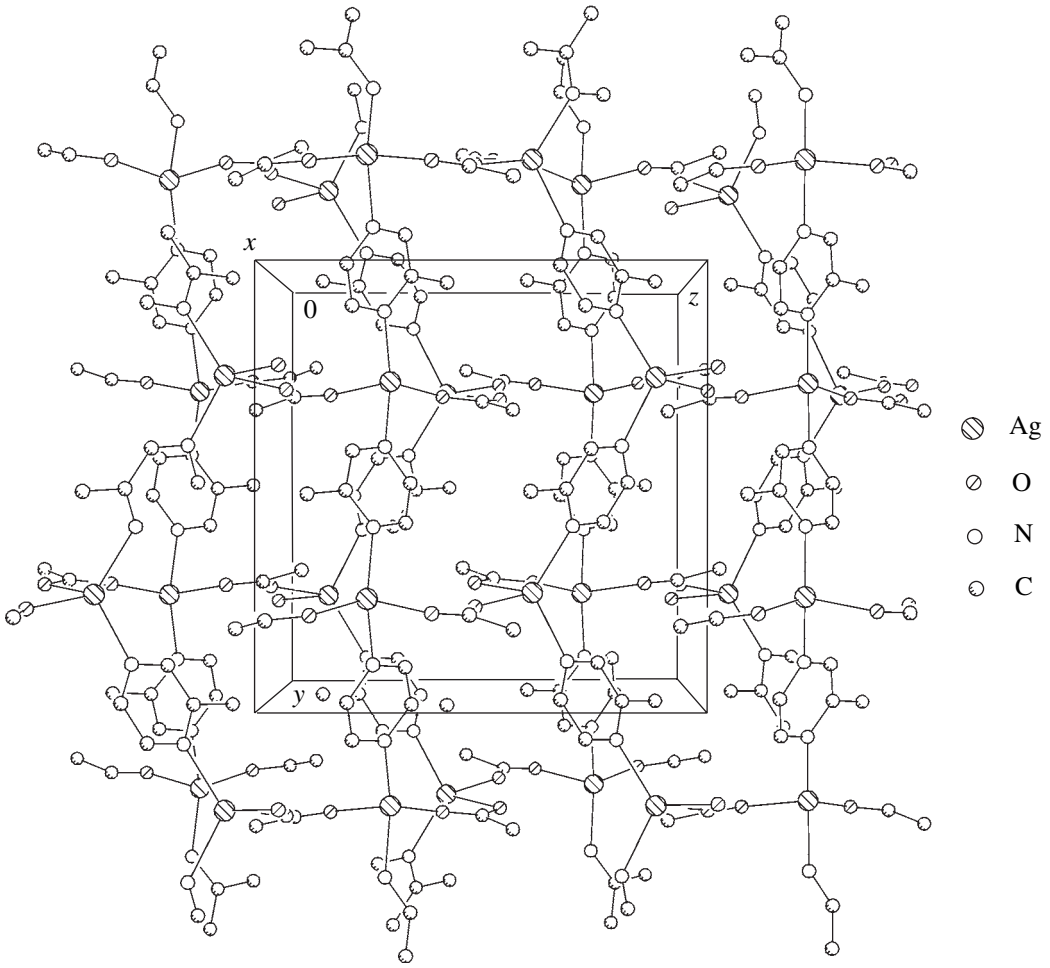

Fig. 1. General view of structure **I** (the F and H atoms are omitted).

RESULTS AND DISCUSSION

The structure of complex **I** consists of the polymer cationic chains of $[Ag(C_5H_6N_2)]^-_\infty$ united into a three-dimensional network through the $CF_3CO_2^-$ anions (Fig. 1). Each of two crystallographically nonequivalent silver atoms (Ag(1) and Ag(2)) has a distorted tetrahedral coordination due to two N atoms of two methylpyrazine molecules and two O atoms of two different CF_3CO_2 groups. The distances Ag–N lie in a range of 2.271(5)–2.311(5) Å, Ag–O change from 2.368(5) to 2.398(6) Å. The angles at the Ag(1) and Ag(2) atoms are strongly distorted and vary within 91.1(2)°–121.1(2)° (Table 3). The molecules of 2-methylpyrazine act as bridges between neighboring Ag ions (Ag···Ag 7.34 Å). As a result of the interaction of 2-Me-Pyz with the Ag(1) and Ag(2) atoms, zigzag chains oriented along the direction [010] are formed. The length of zigzag "wave" is equal to 12.61 Å in both cases; all metal ions lie in its crests and troughs. Note that two zigzag chains occupy different positions and have different orientations of crests and troughs. The chains involving the Ag(1) atoms are oriented along the *z* axis, while the chains incorporating the Ag(2) atoms are directed along the *x* axis (Fig. 2). The chains are united by bidentate bridging $CF_3CO_2^-$ anions (Fig. 3) into a three-dimensional network. The chains in **I** are analogous in shape to the chains in silver nitrate complex with tetrasubstituted pyrazine [Ag(4Me-Pyz)](NO_3) (**II**) we studied previously [4]. However, in complex **I**, as was shown above, all metal ions lie in the zigzag crests and troughs, while in crystal **II**, only half of the Ag^+ ions lie in the zigzag crests and troughs, whereas the other half lie in the middle positions. The structures of **I** and **II** also differ in the type and form of polymer motifs. Complex **I** under study has a three-dimensional structure, while complex **II** forms layers.

Zigzag chains are frequently encountered in coordination polymers, where extended molecules, for example bipyridine in [Cu(4,4'-Bipy) $(MeCN)_2]BF_4$ [5], act as bridging ligands, while the chains have the shapes

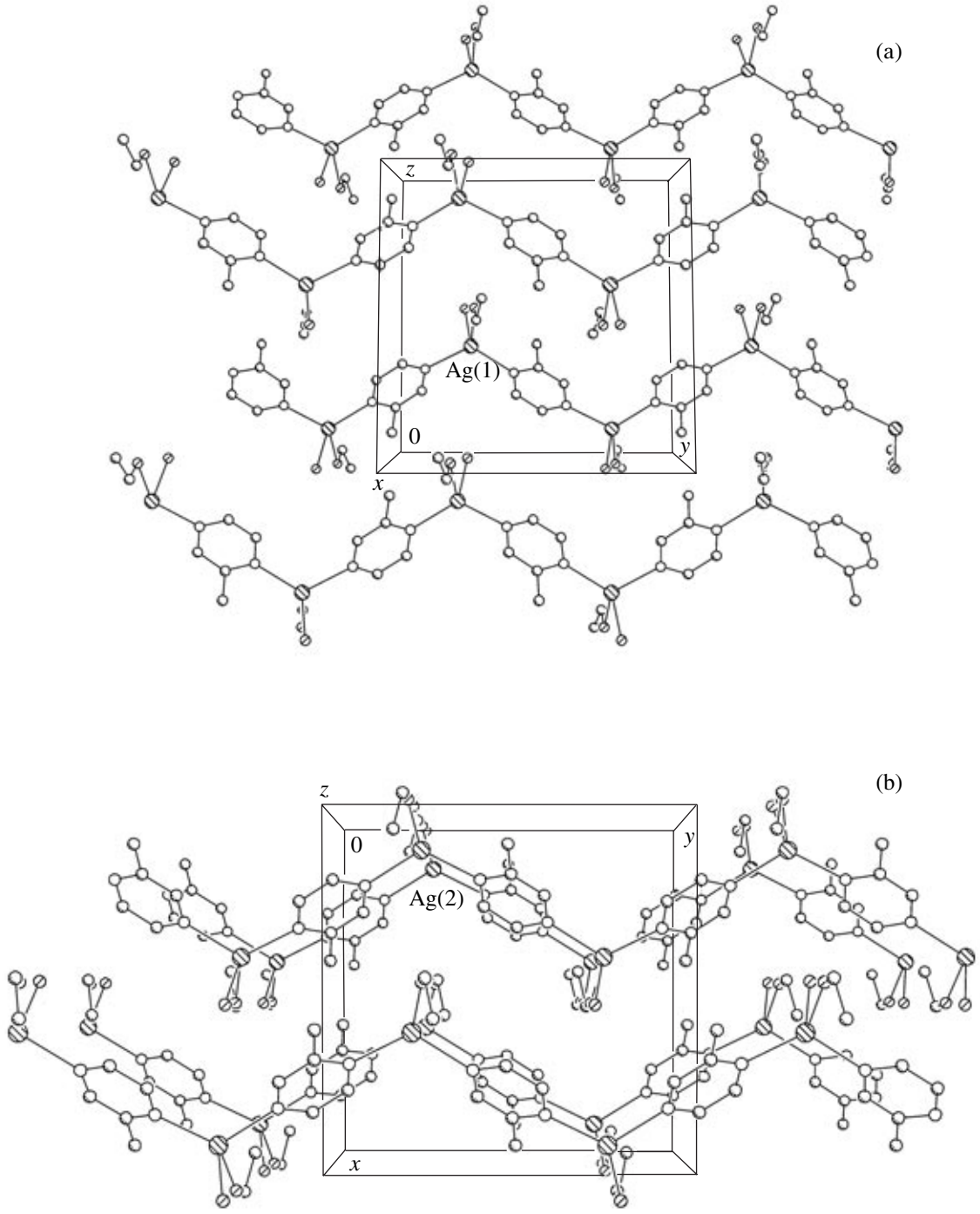

Fig. 2. Zigzag chains of $[Ag(C_5H_6N_2)]_\infty^-$ with participation of (a) Ag(1) atoms and (b) Ag(2) atoms in structure **I**.

analogous to those in complex **I**, where all metal ions lie in zigzag crests and troughs.

The analysis of structure **I** shows that the interaction of $Ag(CF_3CO_2)$ with 2-Me-Pyz results in the rupture of dimeric carboxylate cycle $Ag_2(CF_3CO_2)_2$. At the same time, the $CF_3CO_2^-$ anion retains its bidentate bridging function and links zigzag $[Ag(C_5H_6N_2)]_\infty^-$ chains into a three-dimensional network. Thus, in coordination

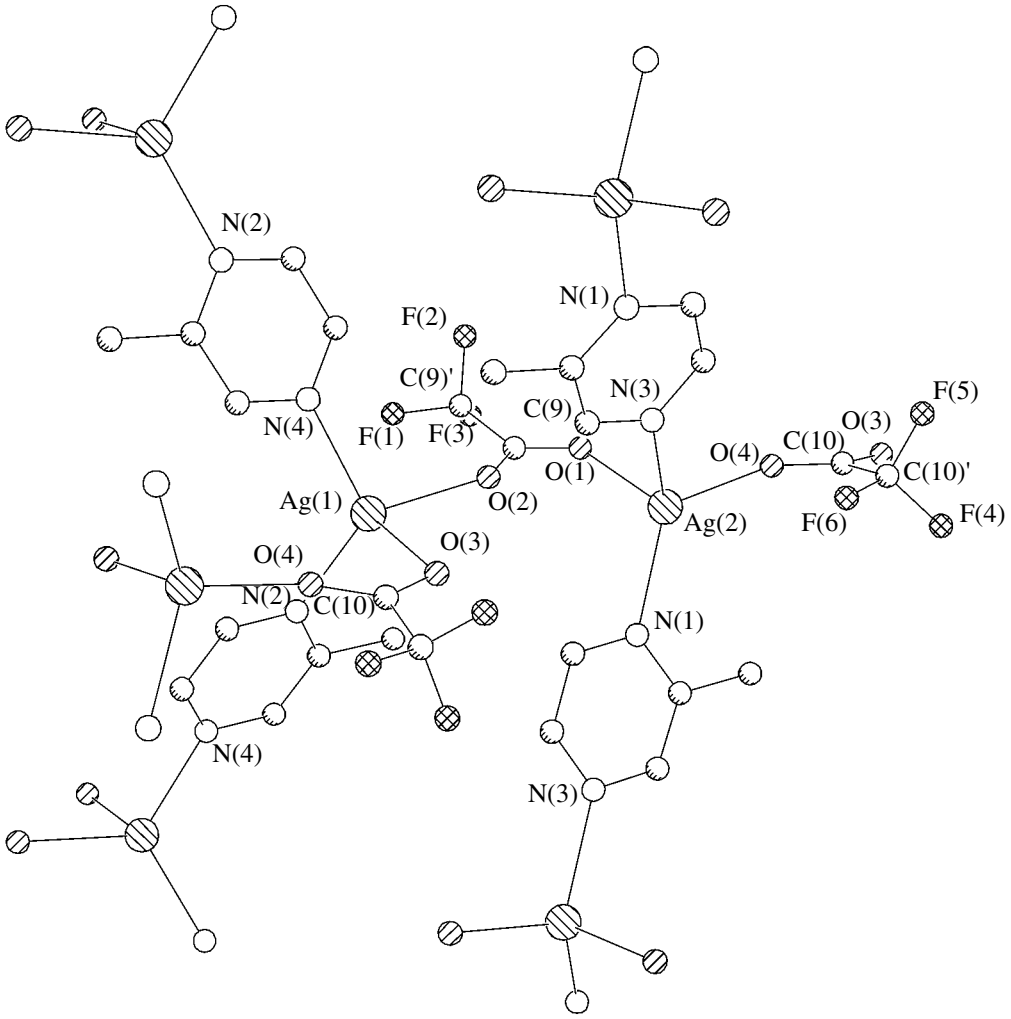

Fig. 3. Fragment of the structure formed by the cationic $[Ag(C_5H_6N_2)]^-_\infty$ chains linked through trifluoroacetate anions.

polymer **I**, both ligands, i.e., the $CF_3CO_2^-$ anion and neutral ditopic 2-Me-Pyz, behave as bridges, which favors the formation of a three-dimensional framework.

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